GE Global Research

Robert Perry
February 22, 2013

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GE … a heritage of innovation

- Founded in 1892
- 300,000 employees worldwide
- $150 billion in annual revenues
- Only company in Dow Jones index originally listed in 1896

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GE today

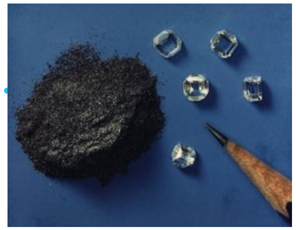
Aligned for growth

Market-focused R&D

- First U.S. industrial lab
- Began 1900 in Schenectady, NY
- Founding principle … improve businesses through technology
- One of the world's most diverse industrial labs

A tradition of innovation

1909 Ductile tungsten
1913 Medical X-ray
1927 First television broadcast reception
1932 Langmuir Nobel Prize in chemistry
1938 Invisible/glareless glass
1942 First US jet engine
1953 LEXAN™ polycarbonate
1955 Man-made diamonds
1962 Semi-conductor laser
1973 Giaever Nobel Prize in physics
1984 Magnetic resonance imaging
1994 GE90® composite fan blade
1999 Digital X-ray
2004 Lightspeed VCT
2009 Wide Bore 1.5T MR System
2010 Energy Smart^{R} LED
2012 Durathon Battery



Expanding our global presence

AMSTC
Ann Arbor, MI

Global Research HQ
Niskayuna, NY

Global Research - Europe
Munich, Germany

China Technology Center
Shanghai, China

Global Software Center
Silicon Valley, CA

Brazil Technology Center
Rio de Janeiro, Brazil

John F. Welch Technology Center
Bangalore, India

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2000 researchers in 7 sites

>3600 patents filed in 2011

Carbon Capture

Technology Development at GE

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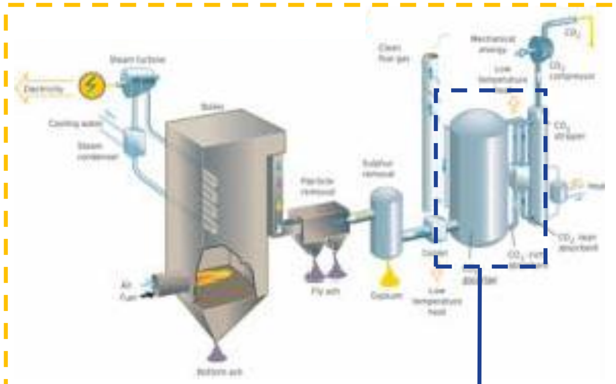
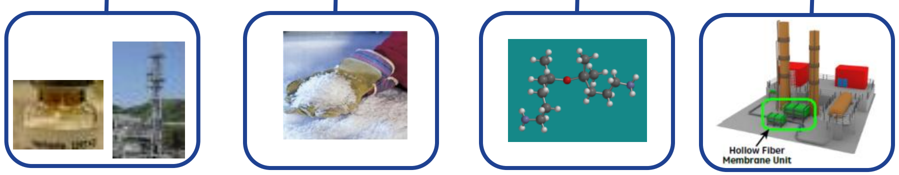
CO_2 Capture Technologies

Post-combustion CO_2 capture



Separation processes



Amine solvent	Low Temp CO_2 Capture	Novel solvent/ Phase Change	CO_2 Selective Membrane
(baseline)	(mid term)	(mid term)	(long term)
Low P CO_2 High steam loss	High P CO_2 No steam loss	Mid P CO2 Low steam loss	High P CO2 No steam loss
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Pre-combustion CO_2 capture

Separation processes

Physical Solvent Selexol™	Temperature Swing Solvents	High Temp H_2 Membrane
(baseline)	(near to mid-term)	(long term)
Low P CO_2 Low T fuel	High P CO_2 Low T fuel	High P CO_2 High T fuel
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Aminosilicone Solvents for Post-Combustion CO_2 Capture

GE Global Research
GE Energy
University of Pittsburgh

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February 22, 2013

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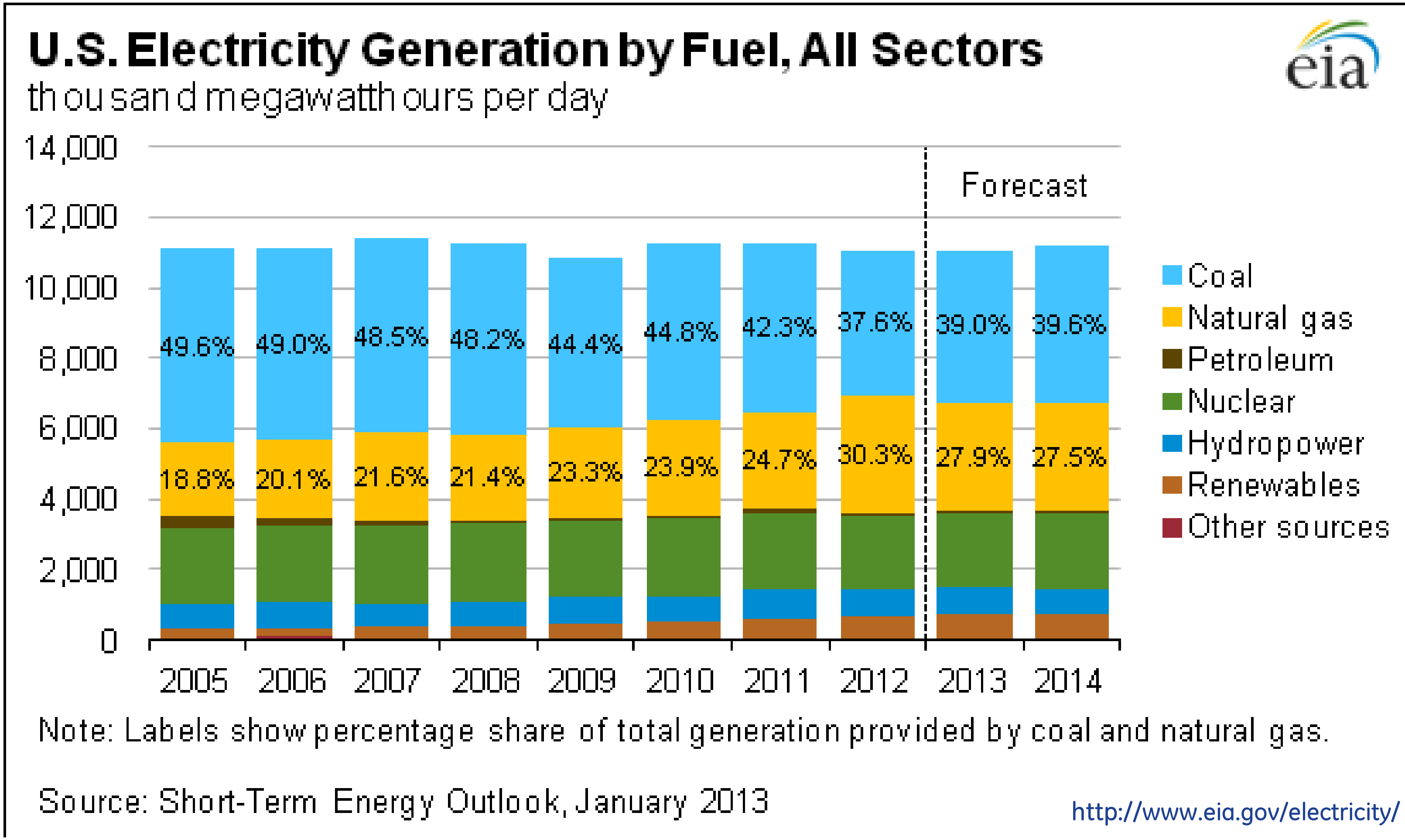
Generation of Electricity

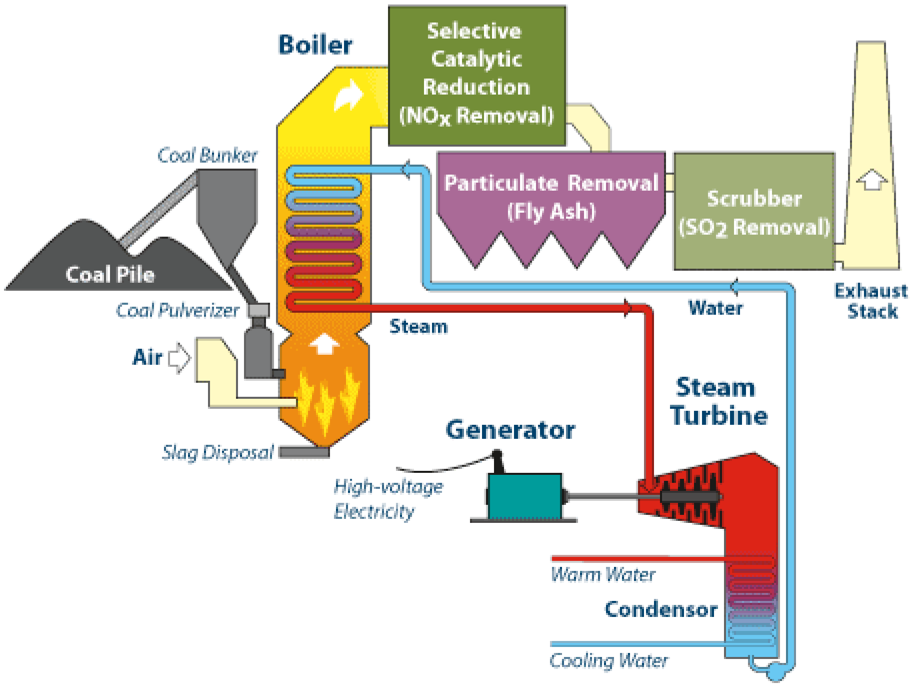


http://www.eia.gov/electricity/

- ~40% of US electricity comes from coal
- This source of power will not be eliminated in near future

Generation of Electricity from Coal

General Process Diagram



- Coal is burned in a boiler to generate steam.
- Steam is used to produce electricity.
- Flue gas from boiler treated to remove solids, NO_x, SO_2.
- CO_2 from combustion currently exhausted to air.

-1400 plants in US produced 318 GW electricity in 2011.
-Also released ~1.7 billion tons of CO_2.

-largest commodity chemical is H_2SO_4 = 60 million tons

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http://www.eia.gov/electricity/capacity/

http://www.ucsusa.org/clean_energy/coalvswind/c02c.html

http://www.topsoe.com/sitecore/shell/Applications/~/media/PDF%20files/Topsoe_Catalysis_Forum/2007/Peacock.ashx

CO_2 Capture & Sequestration

CO_2 Capture- Removal of CO_2 from flue gas.

Potential approaches:

- Chilled ammonia
- Aqueous solutions of organic amines
- Carbonates
- Ionic liquids
- Cryogenics
- Membranes

CO_2 Use & Sequestration- Storage or use of captured CO_2.

Potential approaches:

- Geological storage
- Enhanced oil recovery/fracking
- Artificial photosynthesis
- Reduction to fuel (methanol)

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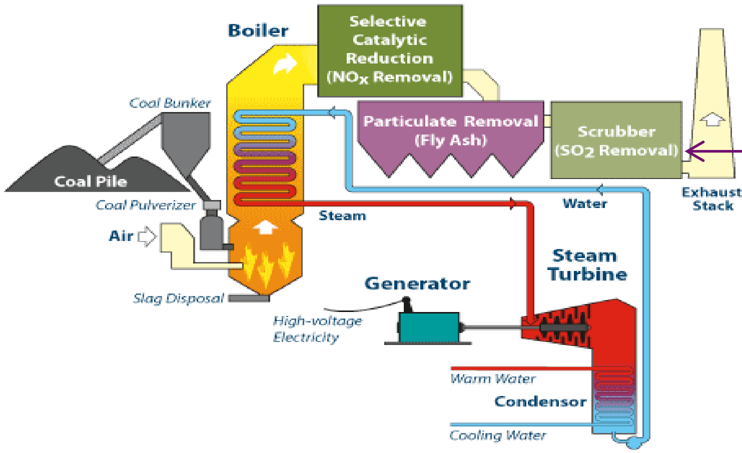
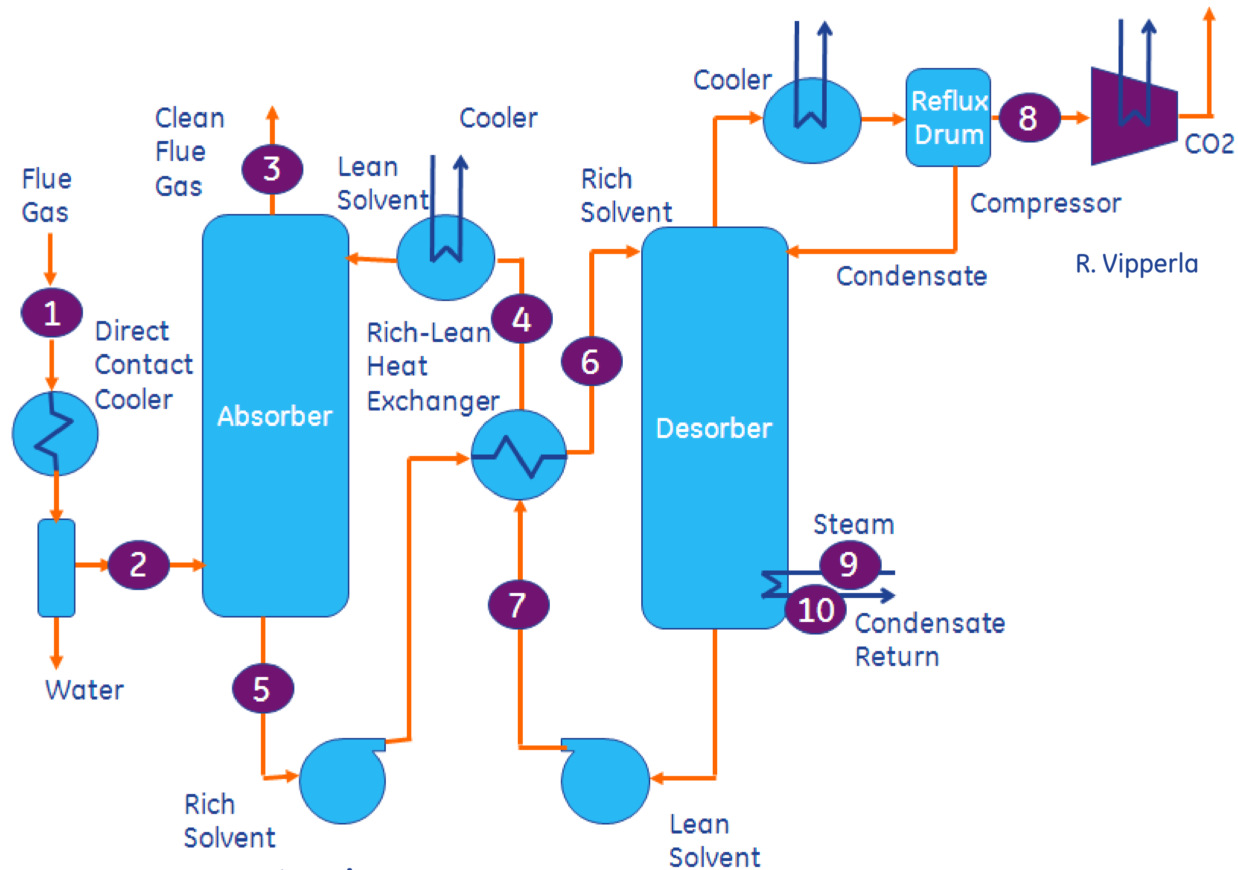
CO_2 Capture Process Schematic



Capture CO_2 after SO_2 scrubber & before stack.

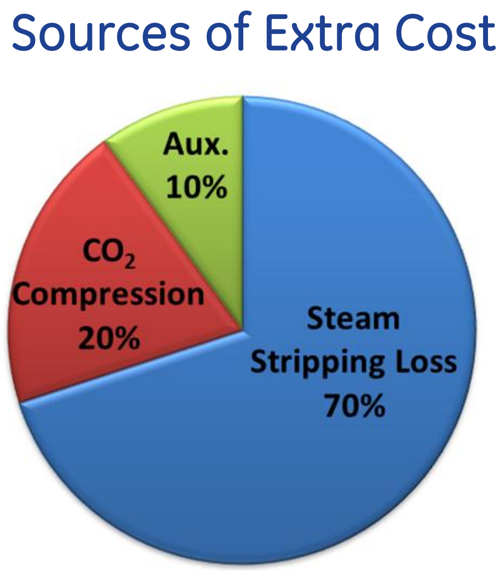
- Absorb CO_2 at 50°C/ 1 atm
- Rich solvent heated to 120 °C to release CO_2
- Lean solvent recycled to absorber
- CO_2 compressed for storage



R. Vipperla

Typical capture process

MEA Process Issue - Cost of Electricity (COE)



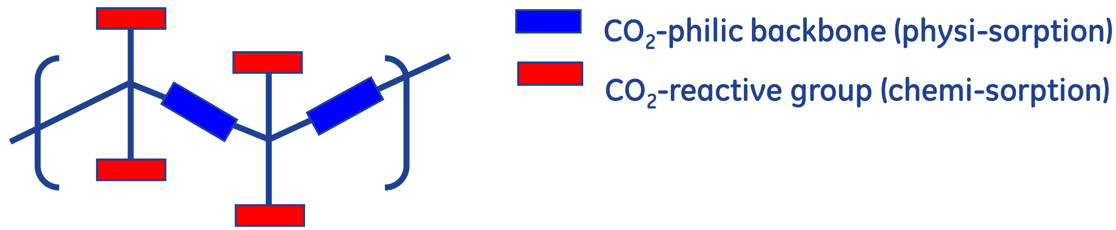
- 30% power lost in conventional MEA process (~80% increase in COE).
- Significant portion of that due to heating/condensing water
- Other issues with MEA:
  - Corrosivity
  - Thermo-oxidative instability
  - Volatility

New Solvent System

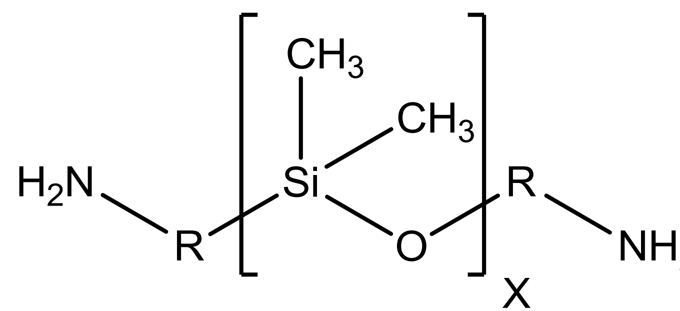
DOE Target: Material & Process with >90% CO_2 capture efficiency & <35% increase in COE vs plant w/o capture

Solvent Properties

- Low/no water
- Liquid carbamate salt
- Thermal stability
- High CO_2 loading
- High desorption pressure
- Low desorption energy
- Low volatility
- High reaction rates
- Low cost

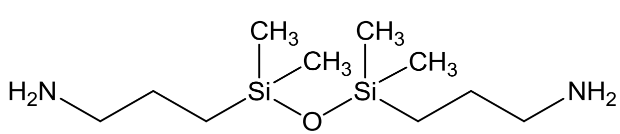


Aminosiloxanes



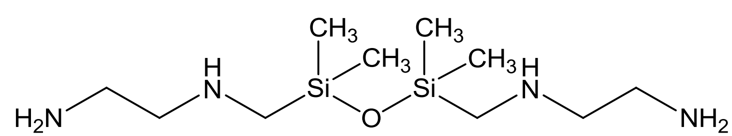
Aminosiloxanes

- High molecular weight amino polysiloxanes used in conditioners for hair & in textile treatment
- Amine content of these commercial polysiloxanes low ➡ little CO_2 capacity
- Need low molecular weight monomeric or oligomeric versions
- Commercially available examples:



Bis(aminopropyl)tetramethyldisiloxane

GAP-0



Bis(aminoethylaminomethyl)tetramethyldisiloxane

GAP-AEAM

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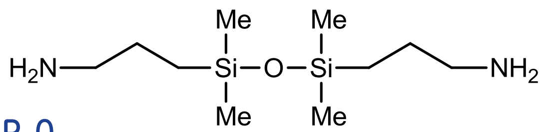
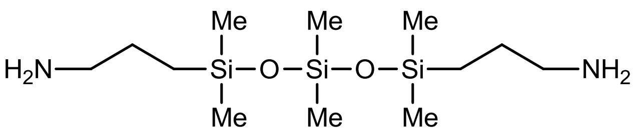
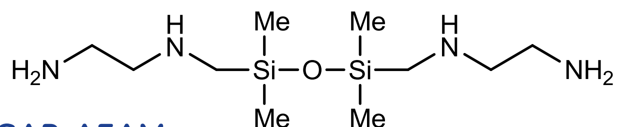
Variety of aminosiloxanes



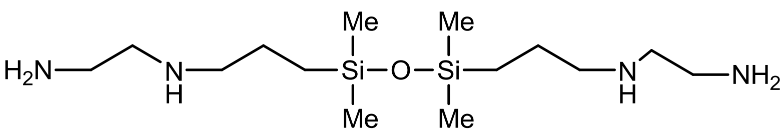
GAP-0



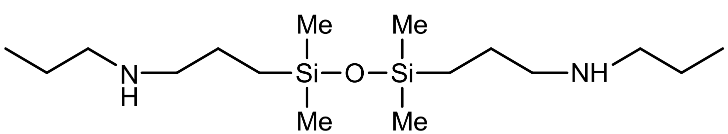
GAP-1



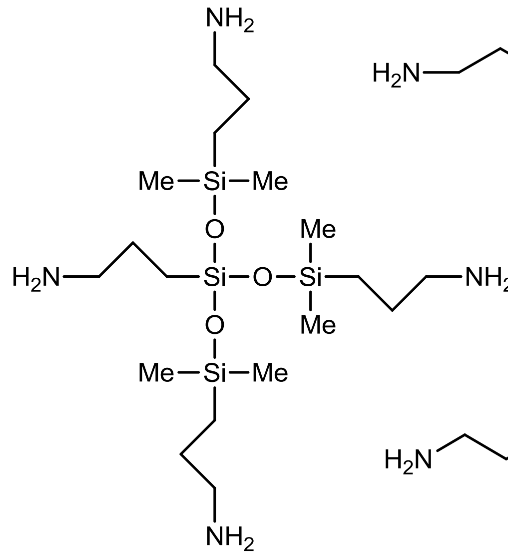
GAP-AEAM



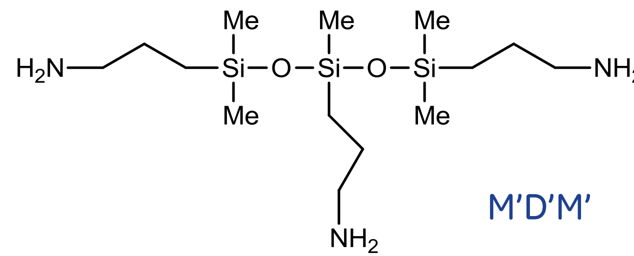
GAP-AEAP



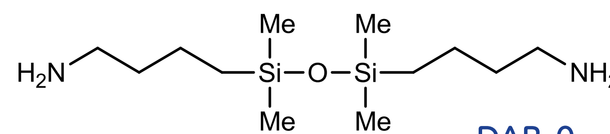
GAP-nPr



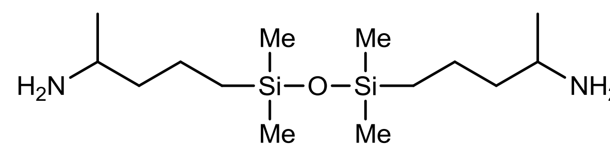
M'₃T'



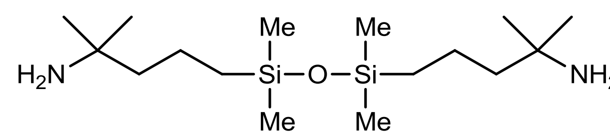
M'D'M'



DAB-0

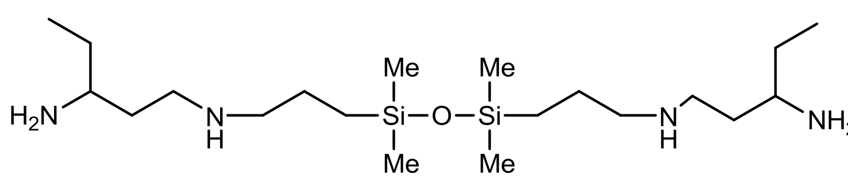


DAB-Me



DAB-Me$_2$

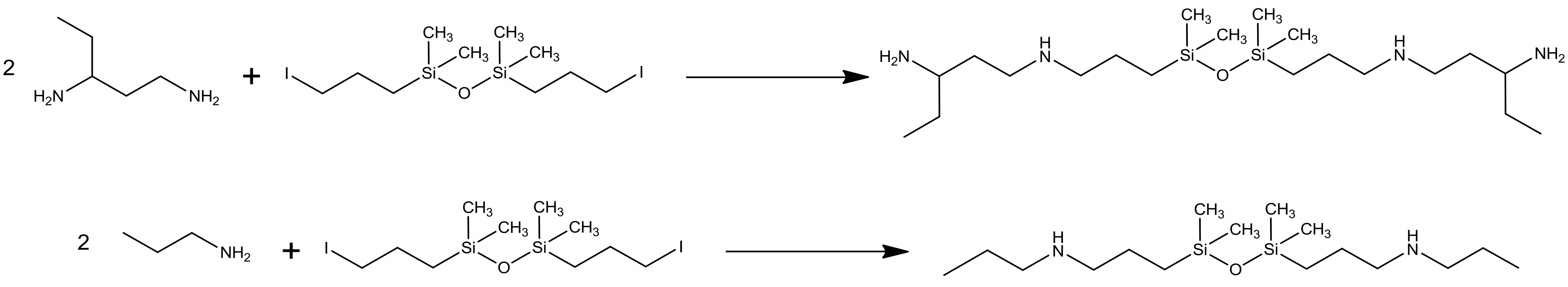
GAP-Dytek



Synthetic Route 1: Alkylation of Primary Amines

$$R\text{-}NH_2 + R'\text{-}X \longrightarrow R\text{-}NH\text{-}R'$$

Examples:



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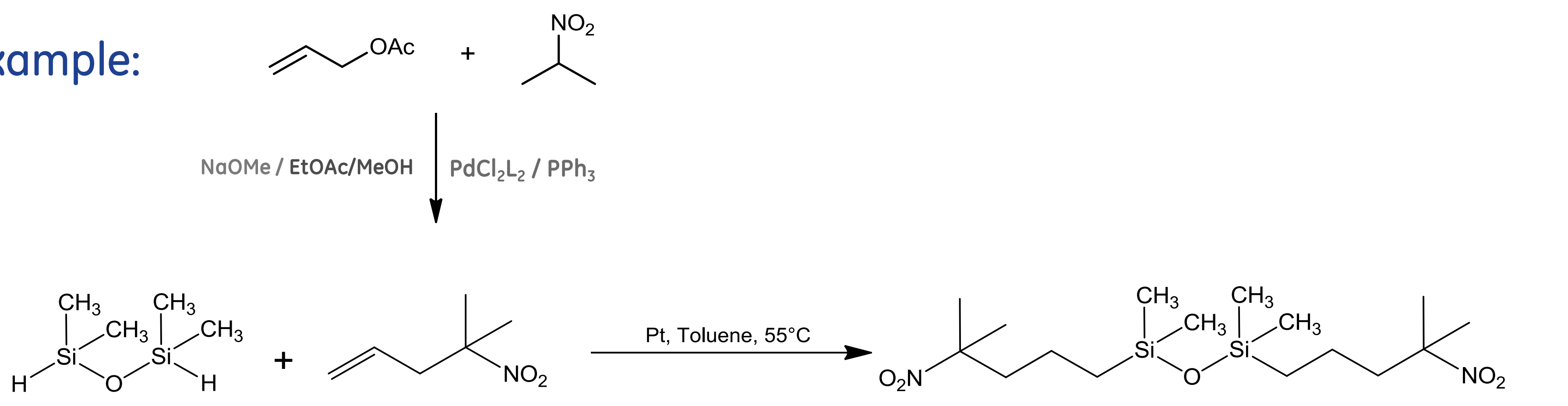
- This method can be problematic => over alkylation is an issue
- Alkyl iodide added to excess amine to mitigate this issue
- Excess amine removed with water washes or vacuum stripping

Synthetic Route 2: Hydrosilylation/Hydrogenation

$$R'_3Si\text{-}H + CH_2\text{=}CH\text{-}R\text{-}NO_2 \xrightarrow{Pt} R'_3Si\text{-}CH_2CH_2\text{-}R\text{-}NO_2 \xrightarrow[Pd/C]{H_2} R'_3Si\text{-}CH_2CH_2\text{-}R\text{-}NH_2$$

Example:



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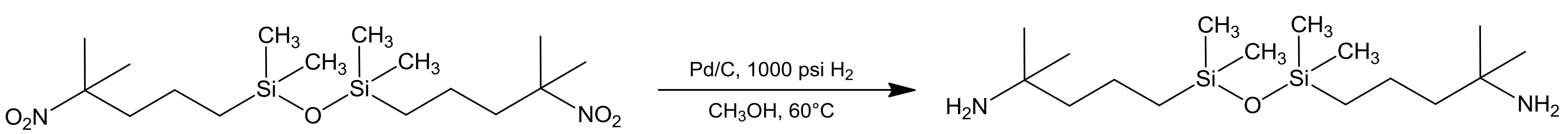
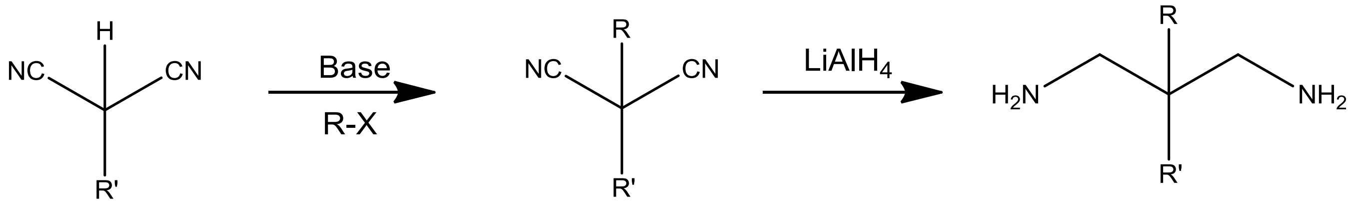
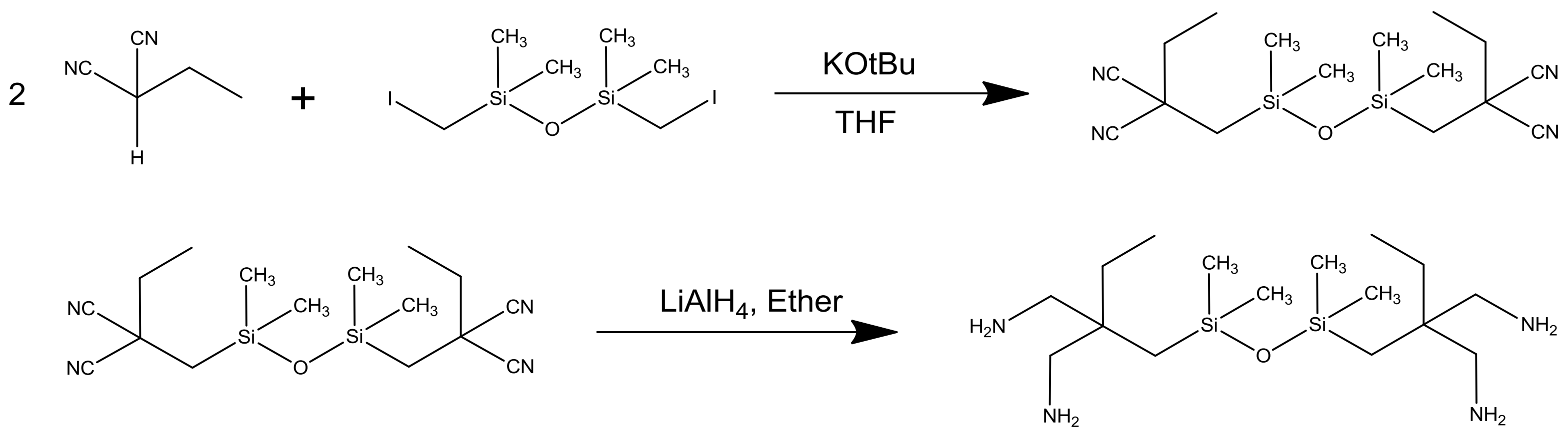


- Hydrosilylation is extremely useful in silicone chemistry.

Synthetic Route 3: Formation of Dinitriles/Reduction



Example:



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- Allows preparation of highly functional compounds

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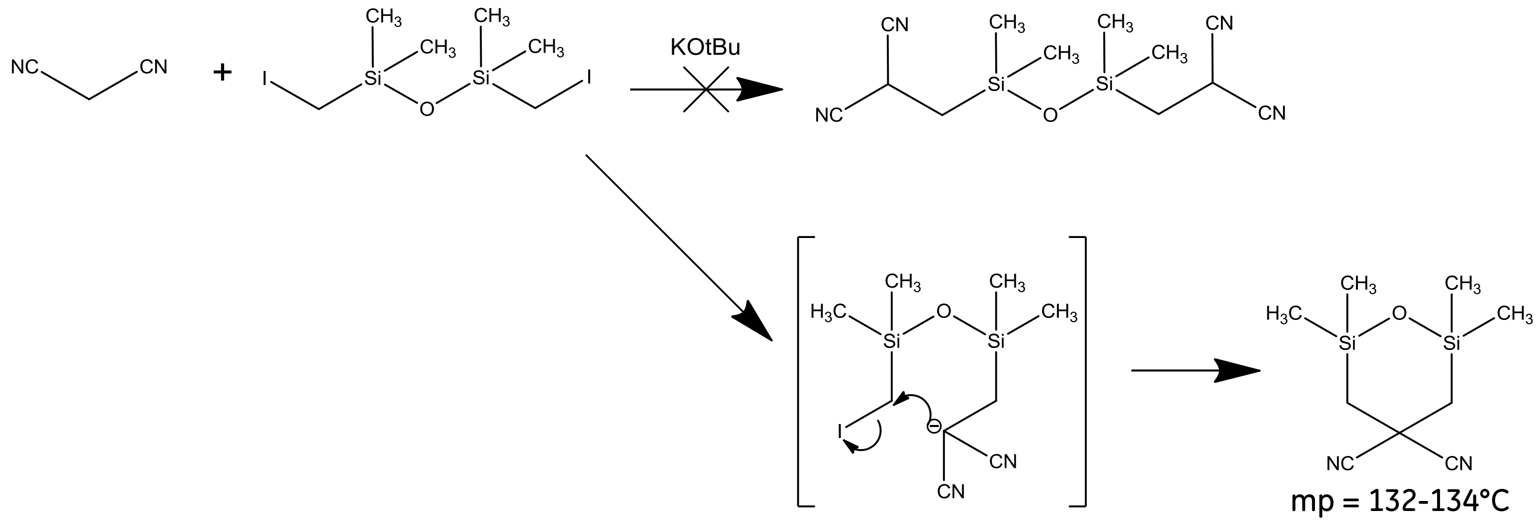
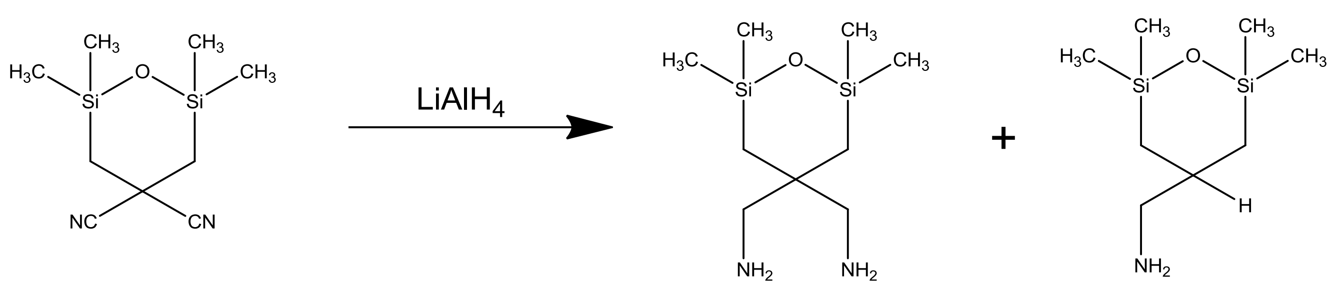
Cyclic Disiloxane Derivatives





Ether/THF	60	40
Ether	98	2

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- Cyclic disiloxane formed instead of linear material
- Some reductive decyanation seen in LAH
- Rxn- solvent dependent

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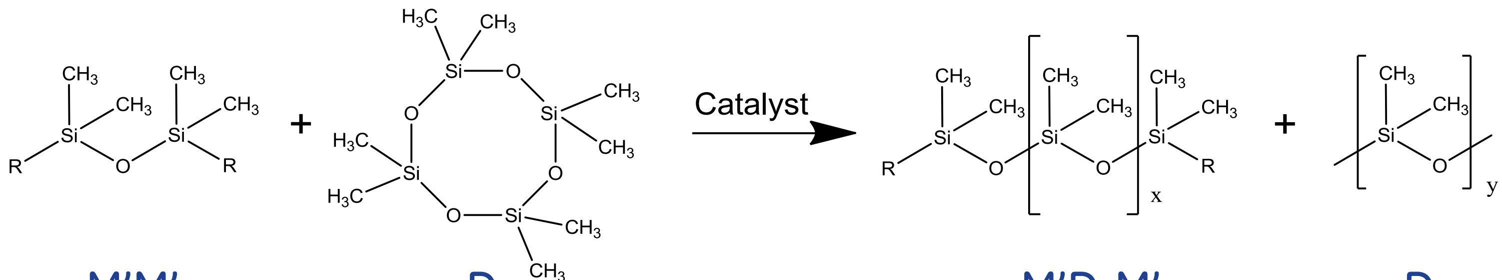
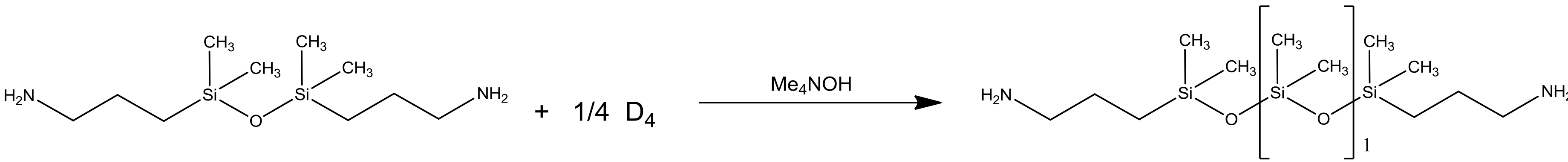
Synthetic Route 4: Siloxane Equilibration



M'M' + D_4 → $M'D_xM'$ (linears) + D_y (cyclics)

Example:

M. O'Brien



GAP-0 → M'DM' (GAP-1)

- Siloxanes mixed and reaction allowed to go to equilibrium
- Catalyst is then removed or destroyed and volatiles (cyclics) stripped
- Can use functional "D" groups as well to control amine content
- Material is actually a mixture of species with average composition equal to target

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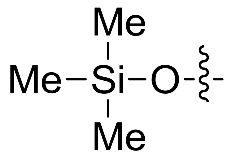
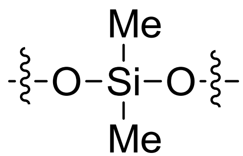
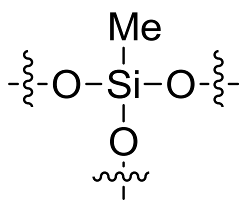
Silicone Nomenclature



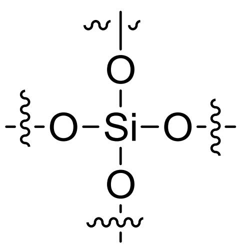
= M



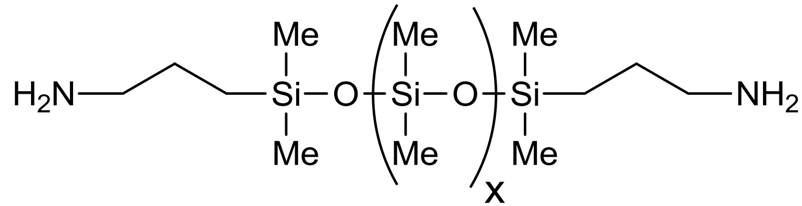
= D



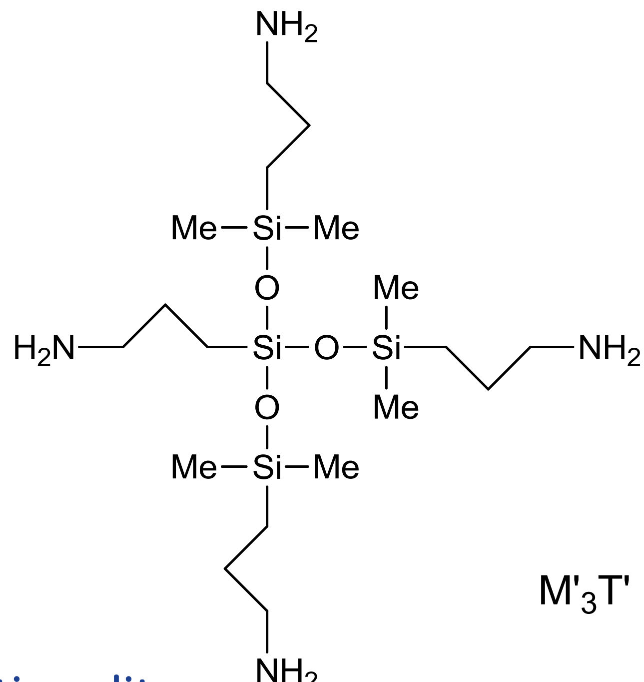
= T



= Q



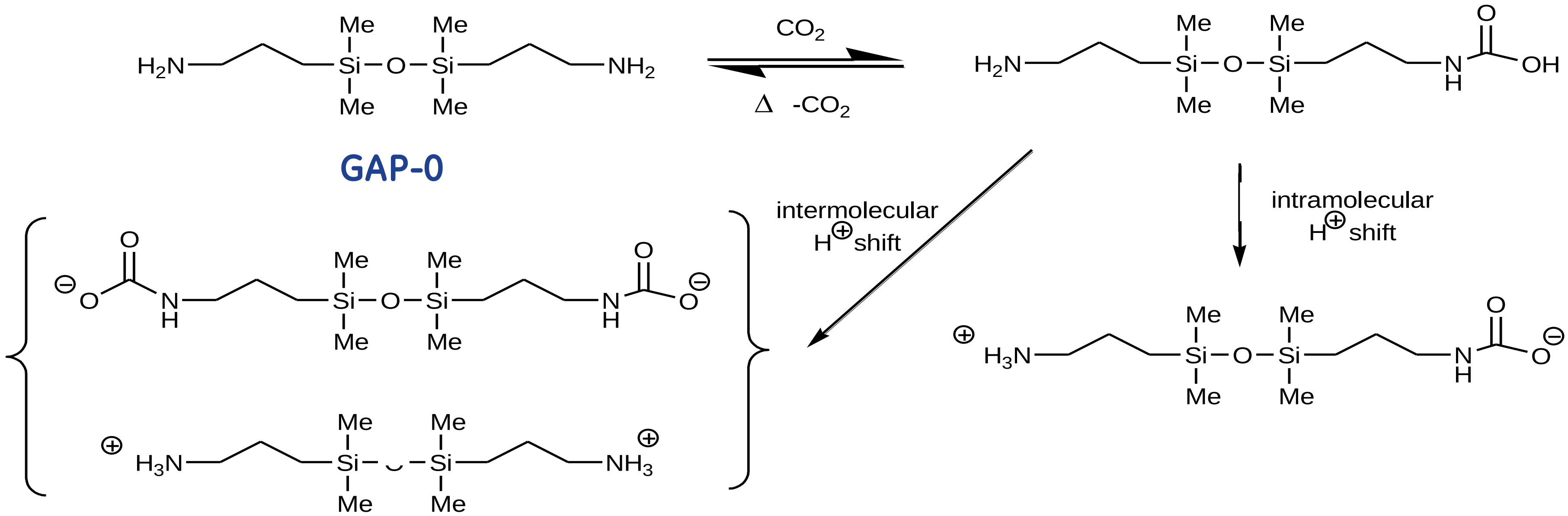
M'DxM'



M'$_3$T'

- Prime denotes functionality

Carbamate Salt Formation with GAP-0

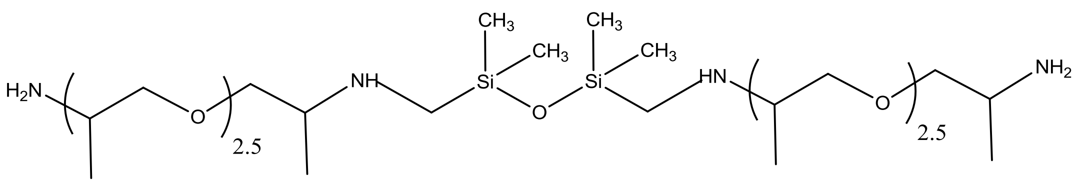


- Absorbs CO_2 very rapidly in the 40-50ºC range
- High CO_2 loading (>17% weight gain, >95% of theoretical value)
- Carbamate readily decarboxylates at higher temps
- However carbamate is solid

Neat Aminosiloxane Summary

- Nearly all aminosiloxanes synthesized gave solid reaction products with CO_2.
  - Depending on nature of solid=> variable CO_2 uptake (mass transfer issues)

- Exceptions were copolymers like:



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- However these materials showed inferior CO_2 uptake (<10% wt gain).
  - Very viscous carbamates => again poor mass transfer tested in bulk

Given that carbamates are mostly solids or very viscous liquids- wanted to test in non-aqueous co-solvents

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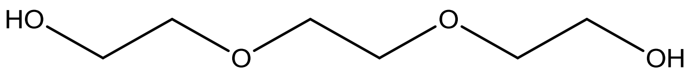
Co-solvent Selection

- Needs to solubilize both aminosiloxane and carbamate at high concentrations
- High boiling to minimize evaporative loss on desorption
- Thermally stable/low toxicity/etc…
- Low specific heat

Best results obtained with ethylene glycol oligomers



Triethylene glycol (TEG)
bp = 126°C/0.1 mm Hg
Specific heat half of H_2O

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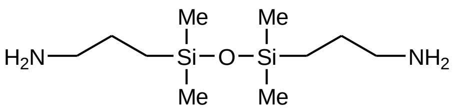
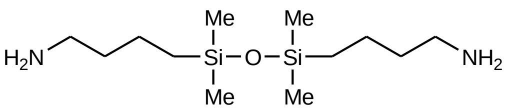
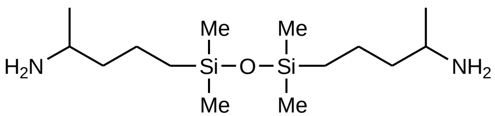
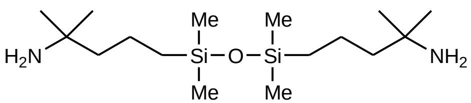
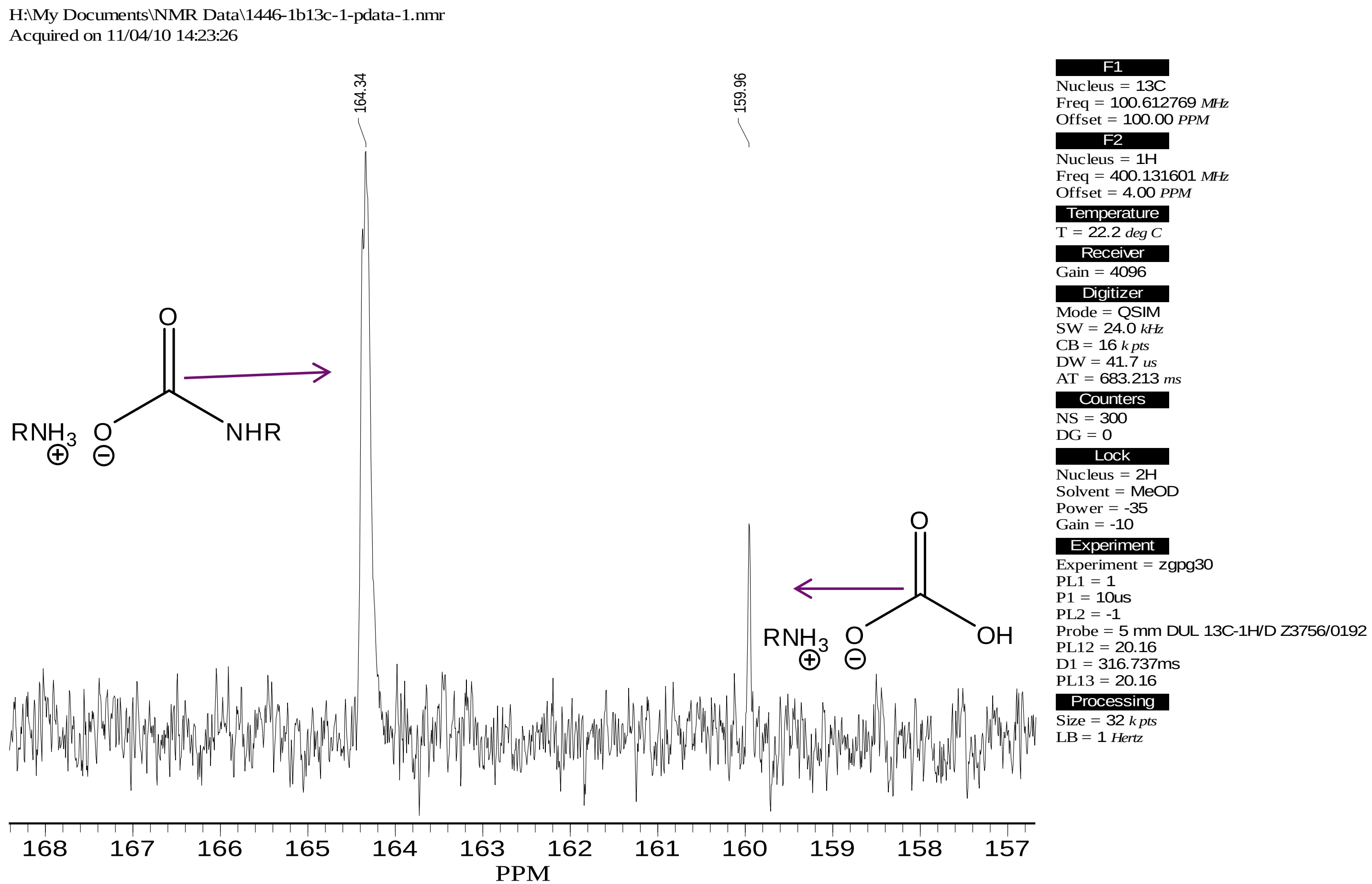
CO_2 Uptake on Diaminosiloxanes

Structure	Neat CO_2 Wt Gain (% of Theoretical)	CO_2 Wt Gain in TEG (% of Theoretical)
	17.3% (98%)	10.2% (115%)
	14.6% (92%)	8.6% (108%)
	13.5% (94%)	8.2% (116%)
	9.5% (72%)	5.4% (84%)

- All 1:1 TEG solutions gave liquid carbamate blends
- Improved mass transfer in liquid => closer to theoretical uptake
- Secondary amine & sterically hindered amine less efficient
- Values >100% theoretical => bicarbonate formation (water in TEG)

$^{13}C\{^1H\}$ NMR of GAP-0/CO_2 Reaction Products

Carbonyl Region



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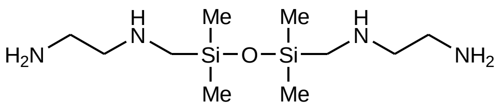
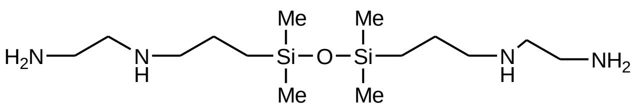
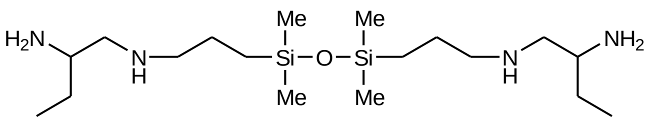
CO_2 Uptake Data: Tetra-aminosiloxanes

Structure	Neat CO_2 Wt Gain (% of Theoretical)	CO_2 Wt Gain in TEG (% of Theoretical)
	21.8% (69%)	15.9% (101%)
	16.7% (64%)	11.8% (90%)
	16.5% (79%)	9.9% (95%)

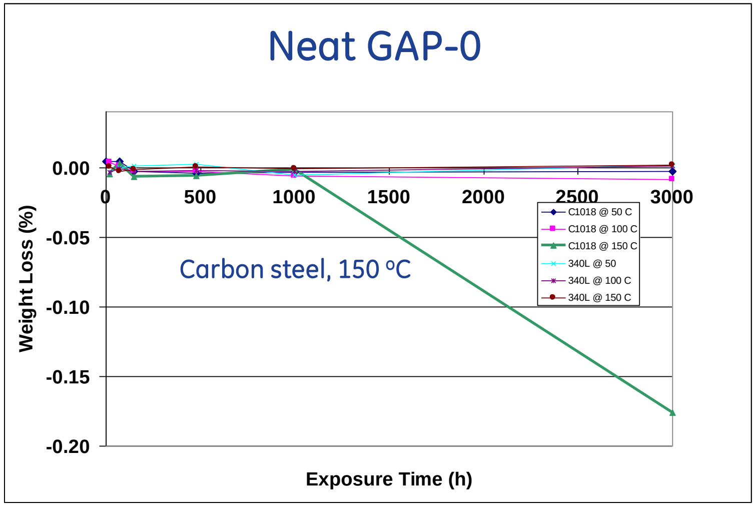
- Tetra-amines: theoretically 2 CO_2's per molecule
- High CO_2 weight gain number neat but not as close to theoretical
  - Half the amines are secondary
  - Solids not as powdery ➡ mass transfer issue
- TEG solutions all liquid, uptake closer to theoretical

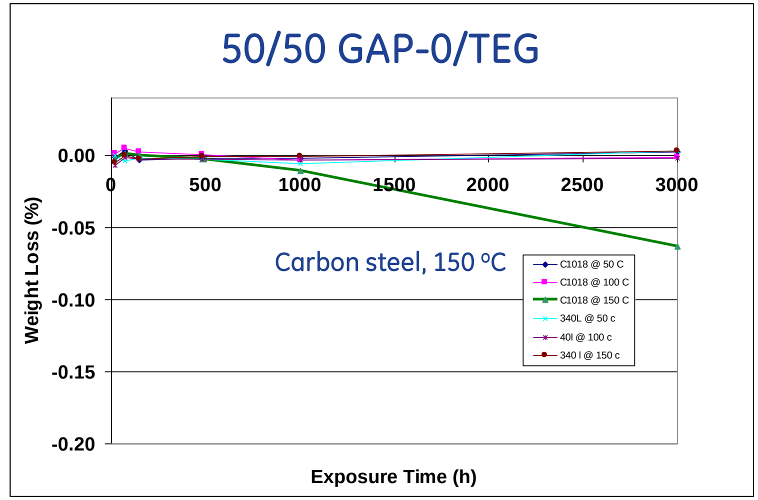
CO_2 Uptake Data: Aminosiloxane Oligomers

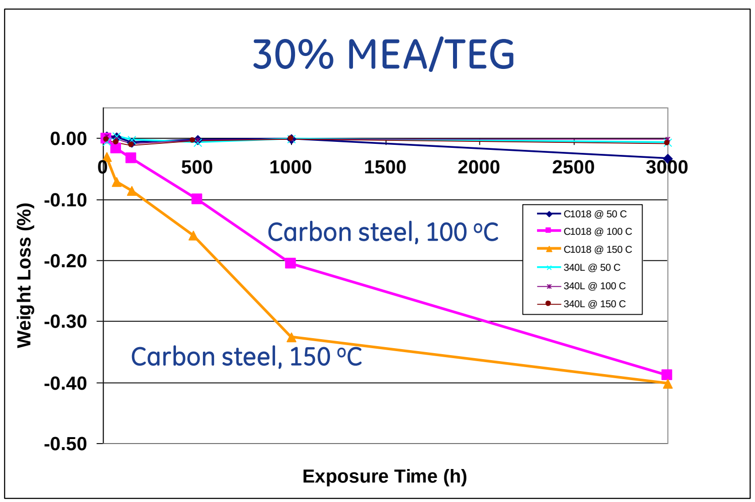
Structure	Neat CO_2 Wt Gain (% of Theoretical)	%TEG Needed Liquid Soln	CO_2 Wt Gain in TEG (% of Theoretical)
M'DM'	13.1% (96%)	30%	10.4% (109%)
$M'D_{2.5}M'$	10.9% (107%)	17%	9.3% (107%)
M'_3T'	18.8% (103%)	50%	9.8% (107%)

- TEG also works well with oligomers
- Most cases less TEG is needed to maintain liquidity
- Advantage of oligomers: stable towards crystallization of carbamate

Corrosion Studies



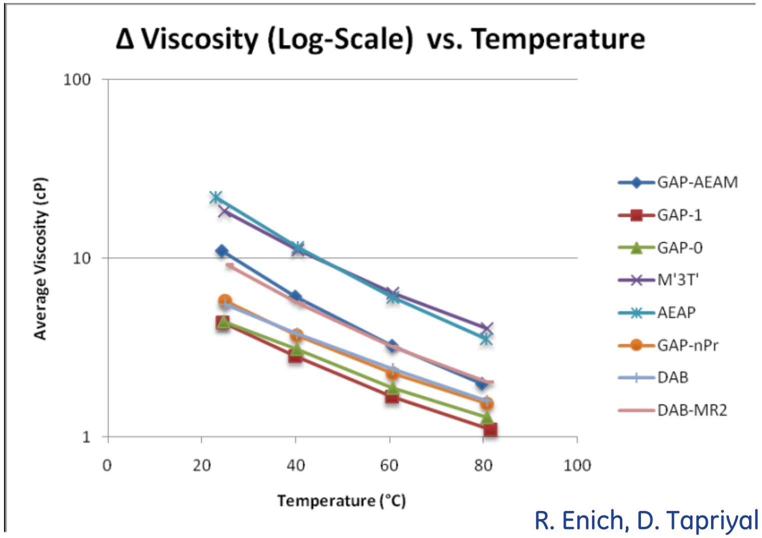




K. Zarnoch

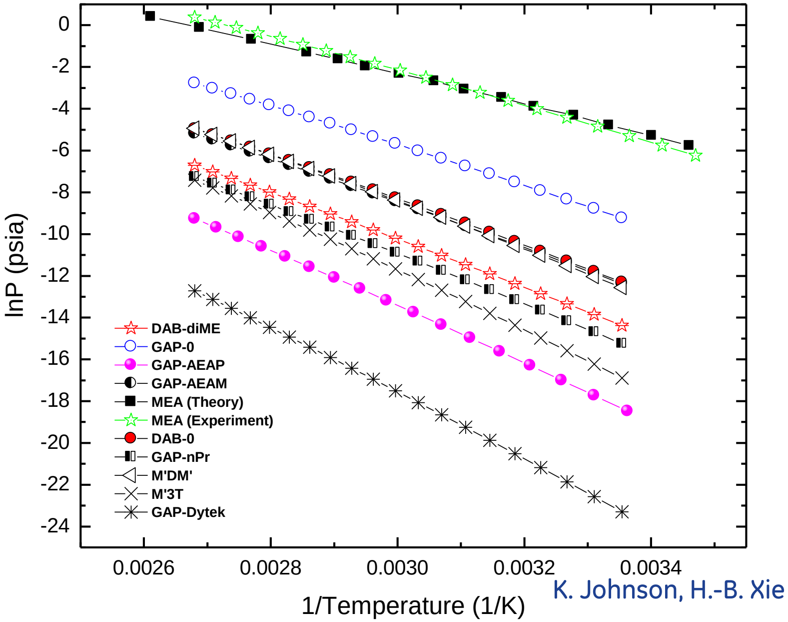
- SS coupons stable in all solvent systems
- Carbon steel stable in neat GAP-0 to 1000 h
- Weight loss/corrosion seen with carbon steel @ 150 °C in GAP-0/TEG and large effect with 30% MEA/TEG @ 100 °C

Physical Properties



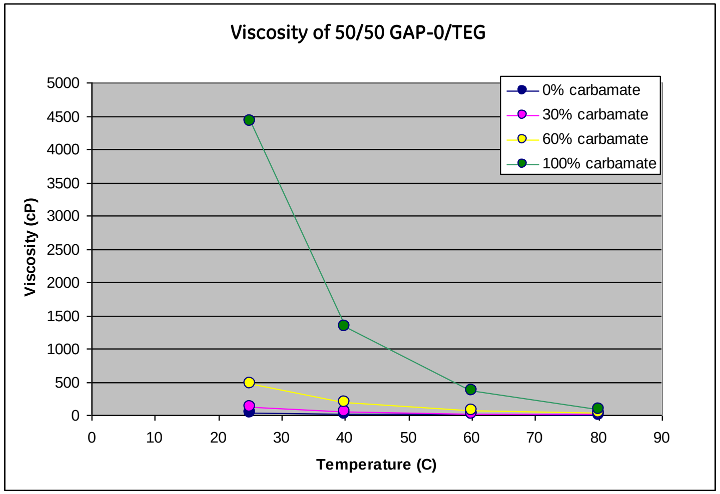
R. Enich, D. Tapriyal

Viscosity

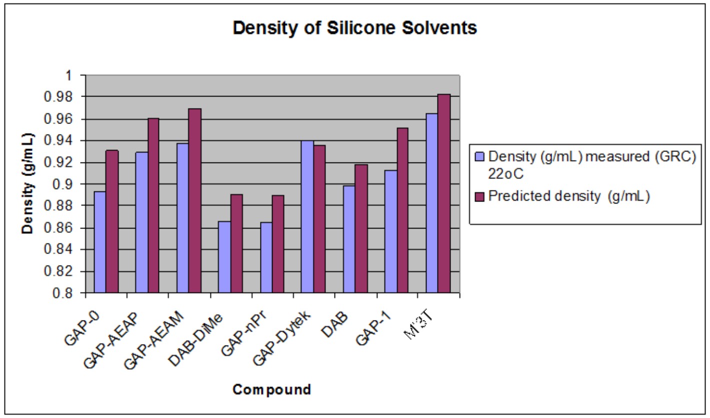


K. Johnson, H.-B. Xie

Vapor pressure



S. Genovese



K. Johnson, H.-B. Xie

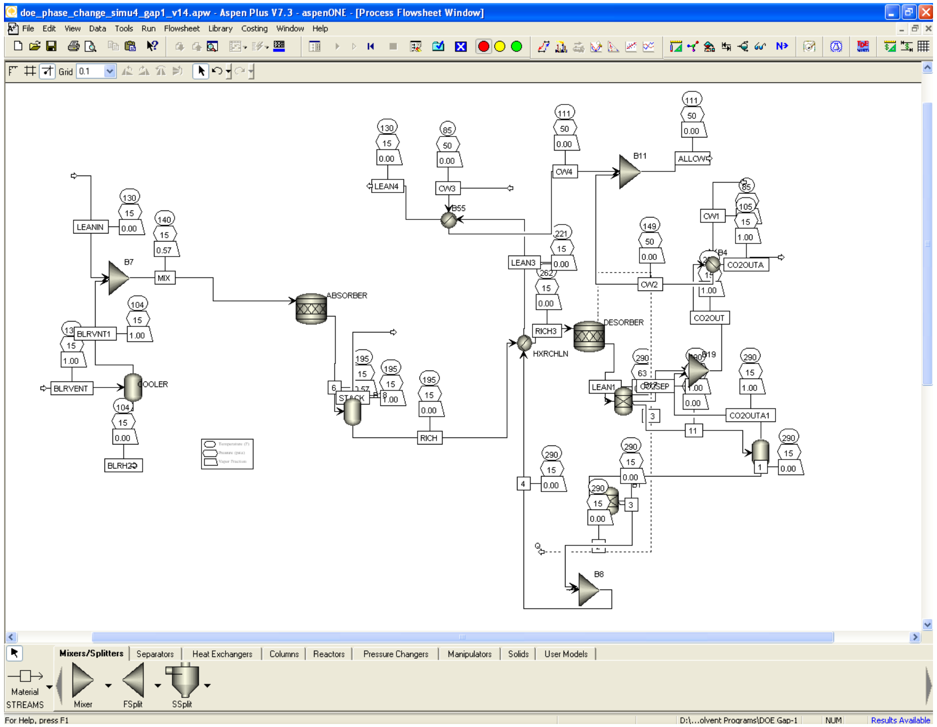
Density

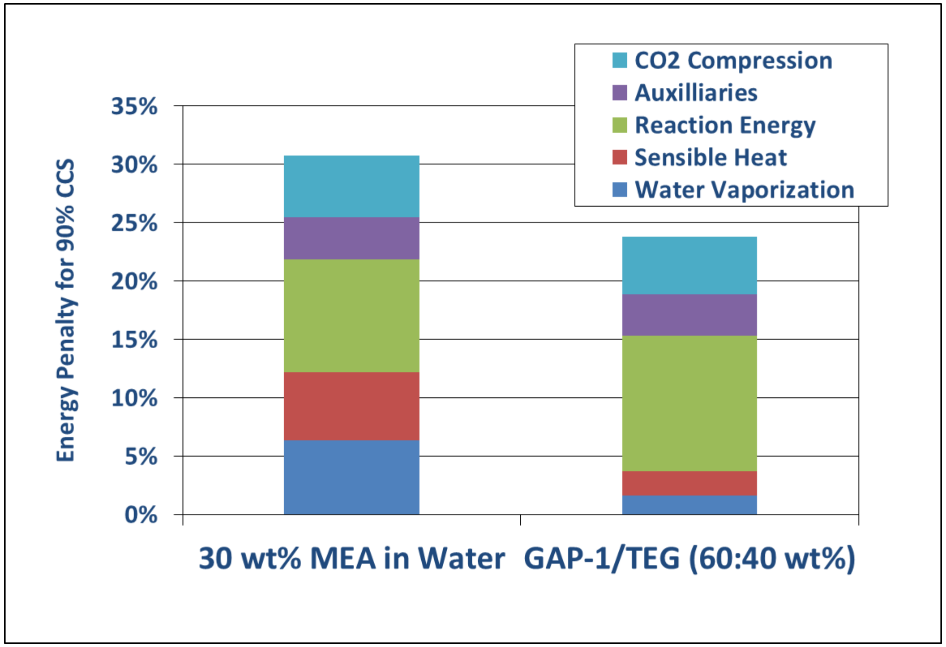
Lab Demonstration of Continuous Process

B. Wood

- Successfully demonstrated with GAP-0 and GAP-1/TEG blend
- Over time GAP-0 carbamate crystallized while GAP-1 version did not

Energy Penalty





- ASPEN Plus model built for CO_2 separation using GAP-1; Updated with experimental results
- Energy Penalty: GAP-1 EP for the overall system ~24% vs. ~31% for MEA

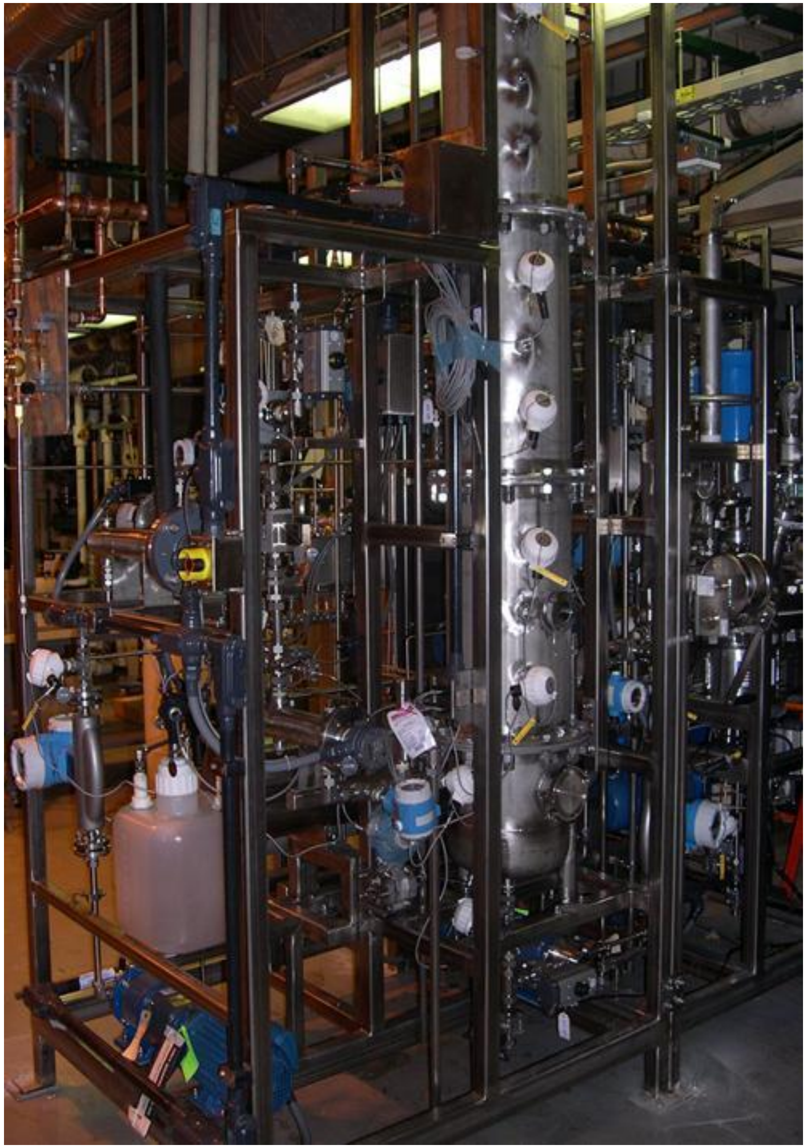
imagination at work

Aminosiloxane/Solvent Blend Summary

- Aminosiloxanes efficiently & reversibly react with CO_2
- Primary amine functionality works best
- Enhanced thermal stability and vapor pressure over MEA
- Polyethylene glycol derivatives like TEG can be used to maintain solution liquidity during CO_2 absorption
- Mass and heat transfer may be mitigated using TEG
- Best candidate currently appears to be GAP-1/TEG

Received additional DOE grant to scale this process up to 80-100X previous lab scale

Bench-Scale Unit



- Fully automated
- Data gathering for pilot scale
- ~100x scale of lab-scale system

ARPA-E Phase Change Program

Program Team

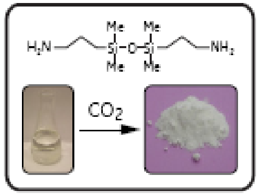
GE Global Research
- Material Development
- Unit Op Design/Testing

GE Energy
- Modeling, and Design of Integrated Energy Systems
- Economic Analysis

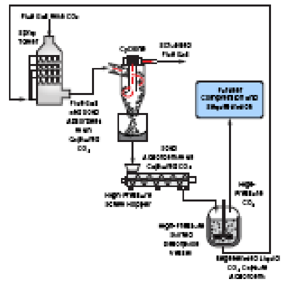
University of Pittsburgh
- Absorption Testing of Materials
- Property Measurement

CO_2 Capture Process Using Innovative Phase-Changing Absorbents, 2 -Year, \$3.8M

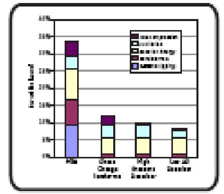
Program Objective: To develop a cost-efficient process that utilizes a CO_2-capture absorbent that reversibly transforms from a liquid to a solid upon reaction with CO_2 to remove CO_2 from flue gas derived from pulverized coal fired power



Material Advancement



Process Development



Plant and Process Modeling

Technical Approach
- Optimize advanced phase-changing absorbent
- Design innovative process integrating absorption of CO_2, transfer of solid material, and desorption of CO_2 under pressure
- Develop and optimize plant and process modeling for unique CO_2 capture process

Program Deliverables
- A material and CO_2 absorption/desorption process that results in <10% parasitic power load and <\$25/ton of CO_2 avoided

Anticipated Benefits of the Proposed Technology
- Eliminate 1 billion tons of CO_2 emissions from PC power plants
- Increase energy security with market for domestic coal
- U.S. leads CO_2 capture technology
- Increase energy efficiency for CO_2 capture vs. MEA
- Create jobs in construction and manufacturing

- 30% power lost in conventional MEA process (~80% increase in COE)
- Significant portion of that due to heating/condensing water
- Low water based processes reduce energy/cost (~50% COE increase)
- Eliminate all non-reactive co-solvents (potential of ~40% COE increase)

Phase-Changing Absorbent

- Almost all neat aminosiloxanes give solid carbamate salts.
- Some were high quality, free-flowing powders
- Those that were powder exhibited high CO_2 uptake.
    - Some >50% higher weight gain than 30% MEA

Could we devise a process to allow use of these materials?

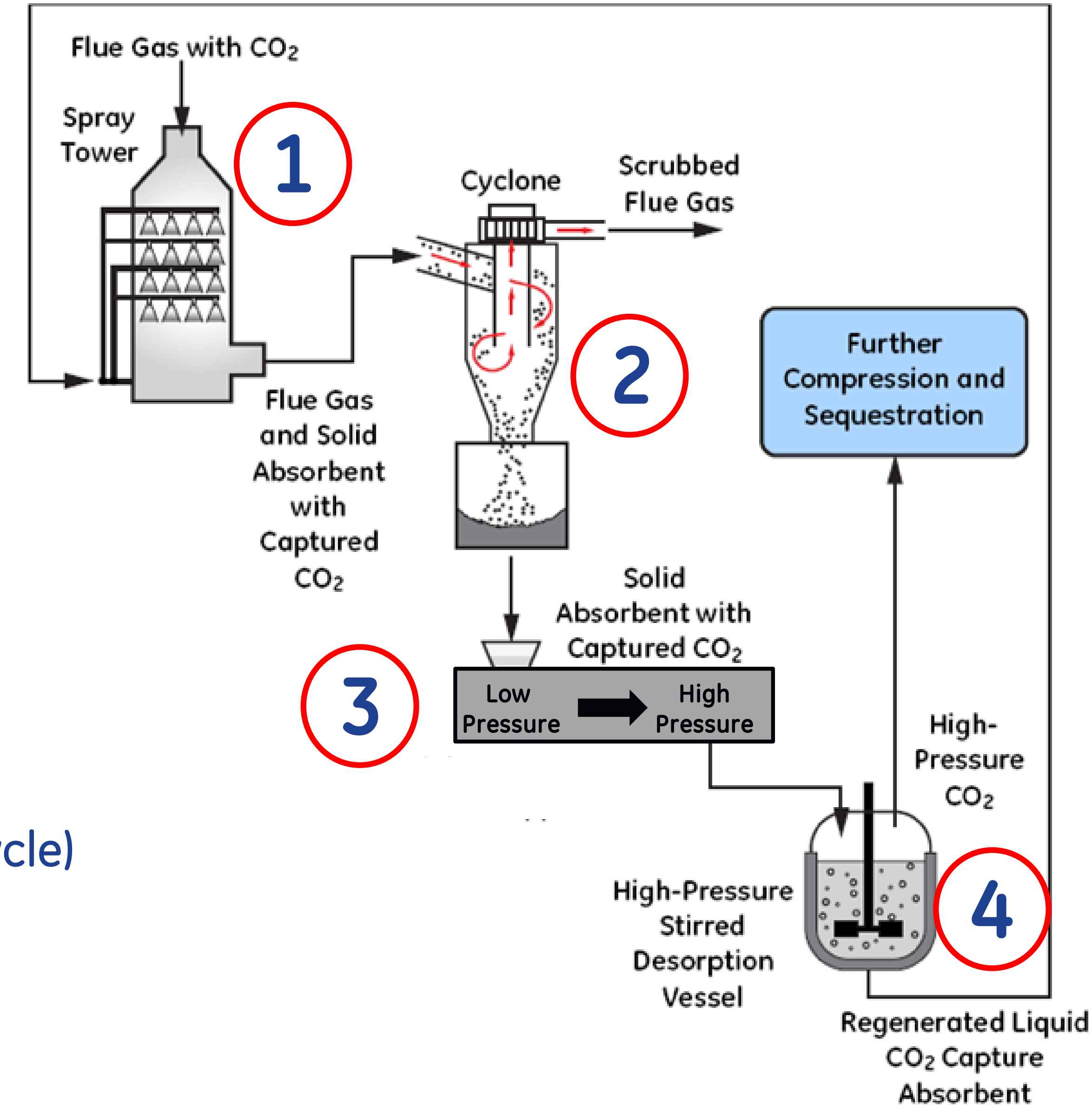
Phase Change Process

1 Make the solid
(Solvent development)

2 Collect the solid
(Solid isolation)

3 Move the solid
(Solids transport)

4 Regenerate the solvent
(CO_2 desorption and recycle)



Solvent Choice for Phase Change Approach

Solvent Requirements

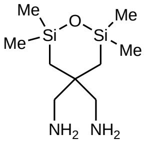
- Low viscosity as liquid
- Highly solid carbamate salt } Free flowing solid
- Low hygroscopicity as salt } Free flowing solid
- High CO_2 loading (≥15% weight gain)
- Low volatility (vapor pressure)
- High reaction rates
- High desorption pressure
- Low desorption energy
- Thermal stability over heat cycles
- Low cost

Need free flowing solid in order to facilitate material collection and transport.

Solvent Evaluation: Form of Carbamate Salt

Studied impact of dry vs wet CO_2

- Dry: CO_2 passed through drying tube before rxn with amine
- Wet: CO_2 passed through H_2O bubbler before rxn with amine.

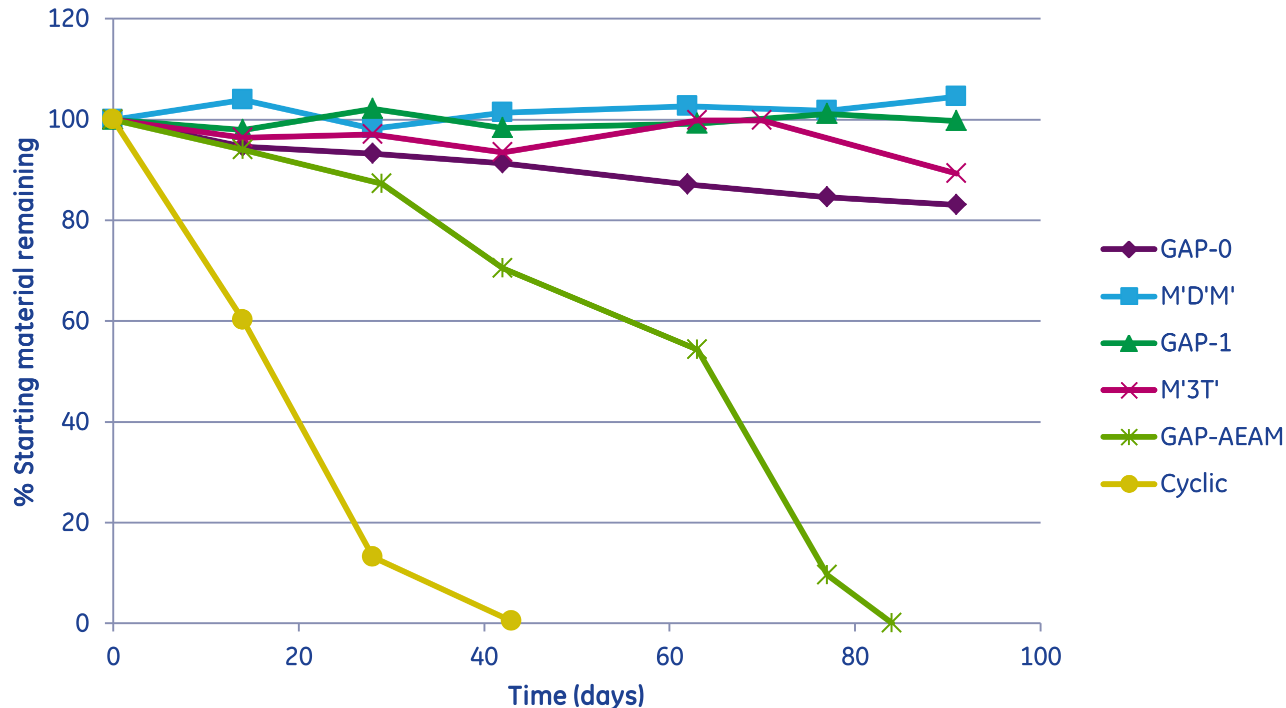
Solvent	Dry % Wt Gain (% of Theoretical)	Dry Salt Form	Wet % Wt Gain (% of Theoretical)	Wet Salt Form
GAP-0	17.3 (98)	Powder	18.4 (104)	Chunky Solid
GAP-1	13.1 (96)	Powder	14.1 (103)	Sticky Wax
M'D'M'	17.8 (99)	Powder	16.6 (92)	Glass
M'_3T'	18.8 (103)	Powder	17.4 (96)	Sticky Gum
	17.3 (92)	Powder	20.7 (109)	Powder

M. O'Brien

- Pure compounds GAP-0 & cyclic diamine looked best
- Oligomer-based salts softened with H_2O & became sticky

Thermal Stability

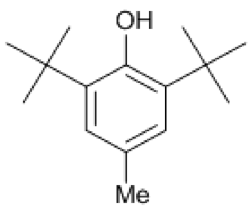
Determine inherent stability by heating to 150°C for 3 months



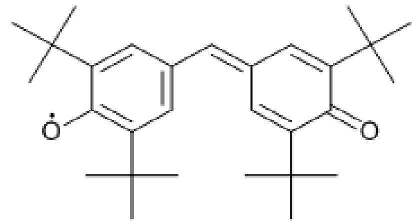
R. Farnum, M. O'Brien

- Many materials show good inherent stability
- Cyclic diamine and GAP-AEAM are exceptions
- Studying decomposition products to provide insight into potential stabilization approaches (additives are commonly used in these systems)

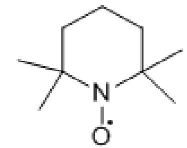
Thermal Stability



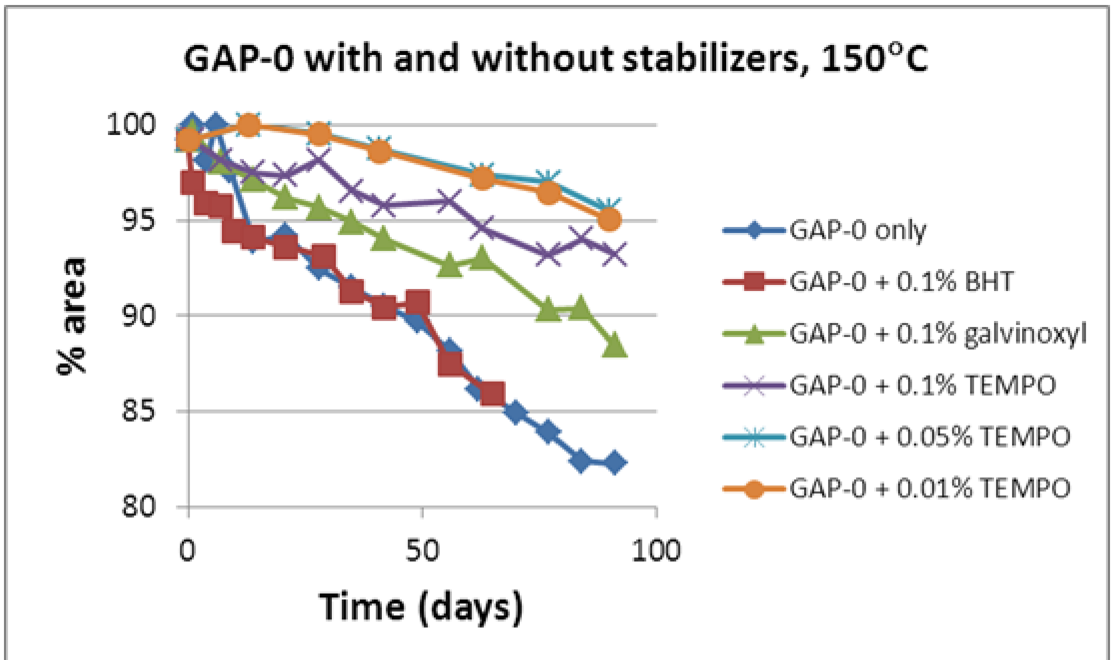
BHT



galvinoxyl

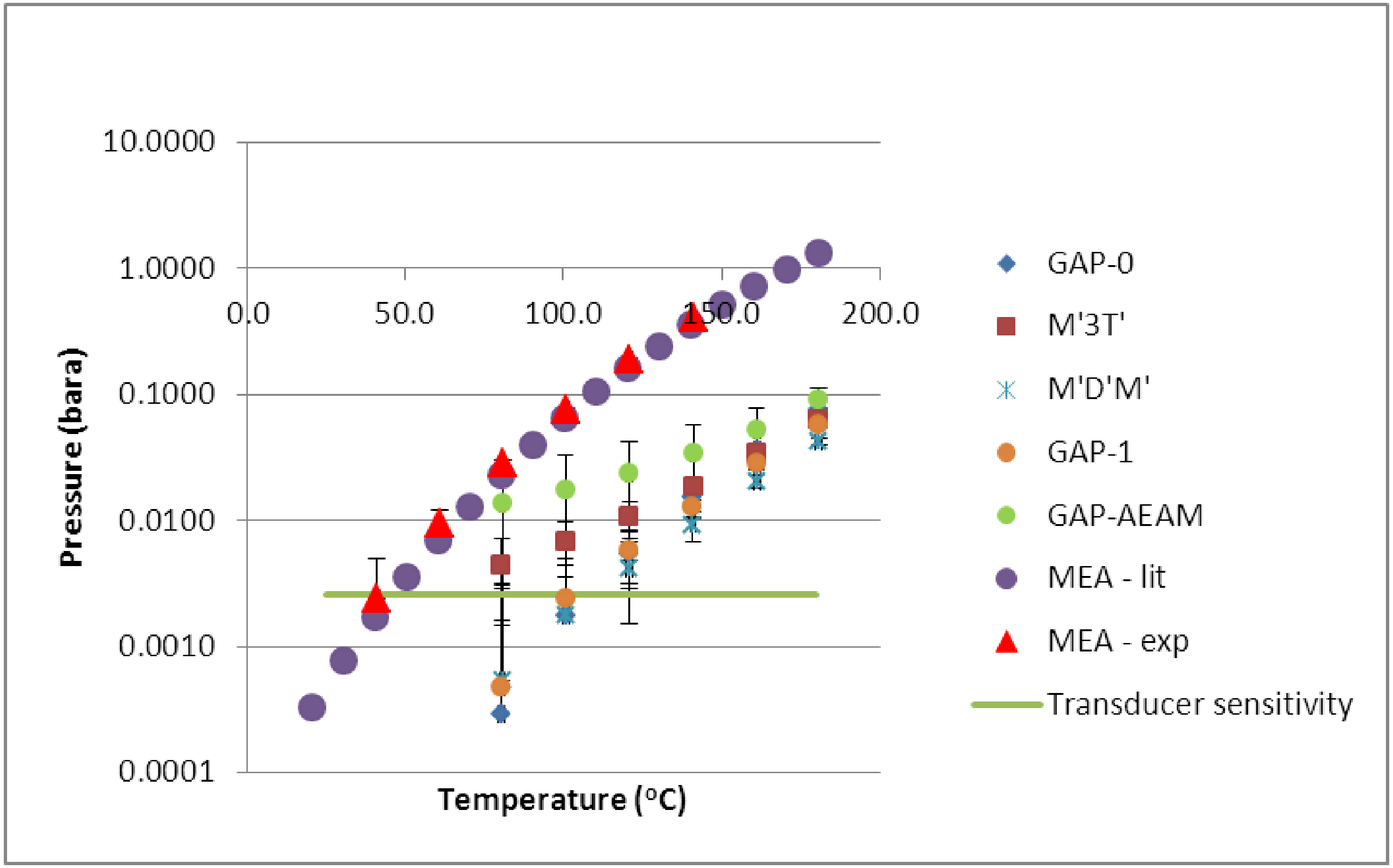


TEMPO



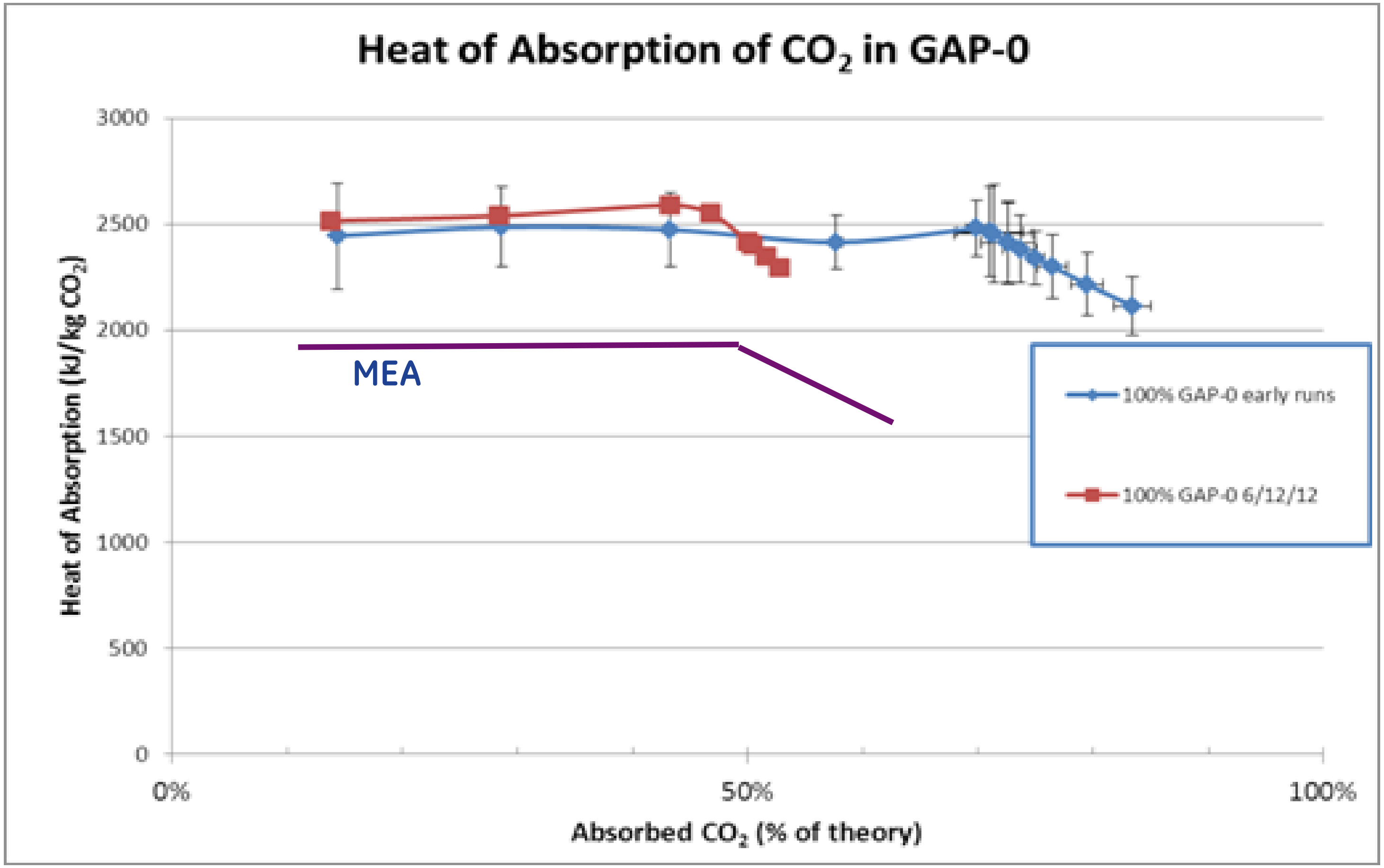
- Significant increase in stability with TEMPO

Vapor Pressure



- MEA control shows excellent agreement with literature
- 1- 2 orders of magnitude reduced vapor pressure vs MEA

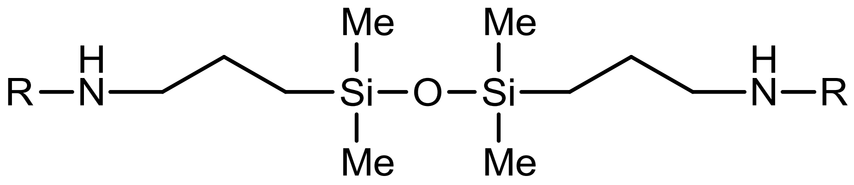
Heats of Reaction



R. Farnum

- GAP-0 ΔH_{rxn} ~ 2500 kJ/kg
- MEA ~ 1850 kJ/kg
- Breaks in curve indicate transition to physical absorption of CO_2

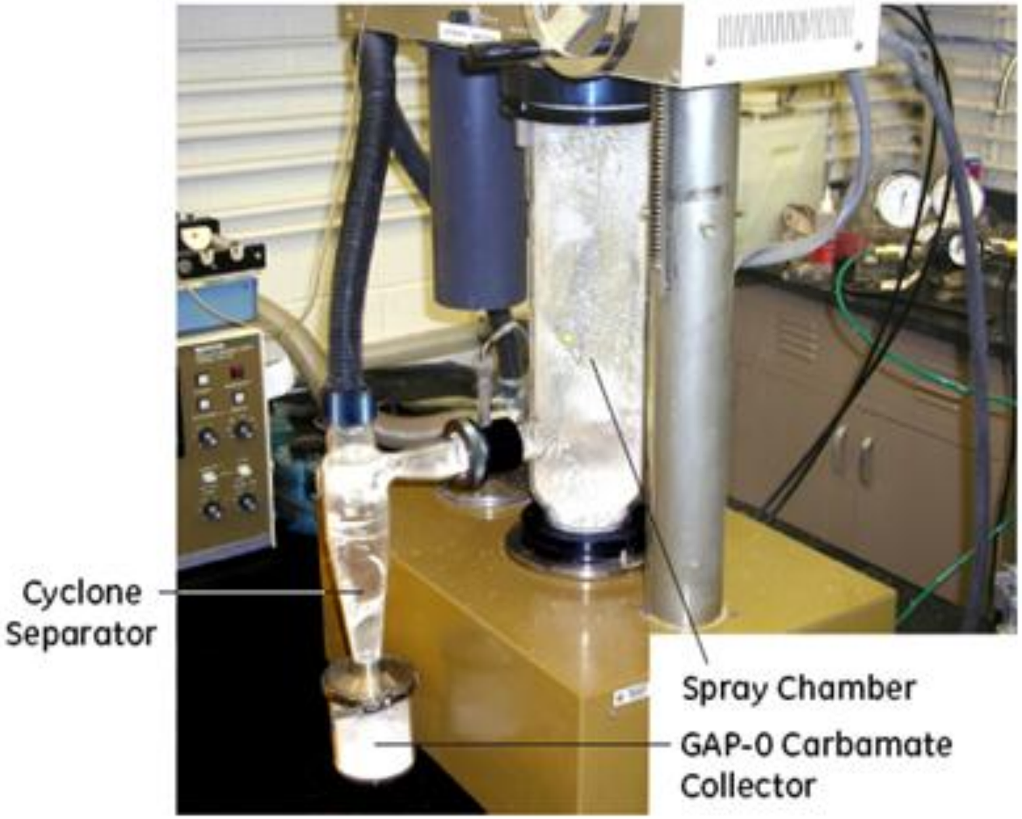
Heats of Reaction



Comp'd	R	% Wt Gain	% of Theory	Heat of Absorption (kJ/kg CO_2)
GAP-0	H	17.3	100	2554
1	Methyl	18.3	115	2168
2	Ethyl	16.5	114	2151
3	Propyl	14.3	108	2125
4	Isopropyl	6.1	46	2026
5	Butyl	13.1	107	2175
6	Isobutyl	10.8	89	2013
7	t-Butyl	0.6	5	ND
8	Cyclohexyl	8.5	85	2035

- Substantial decrease in ΔH_{rxn}
- All material were viscous liquids or pseudo-solids

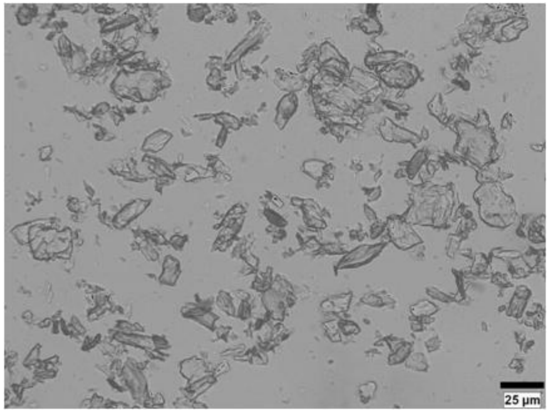
Solid Formation and Isolation



B. Enick
D. Tapriyal
L. Hong

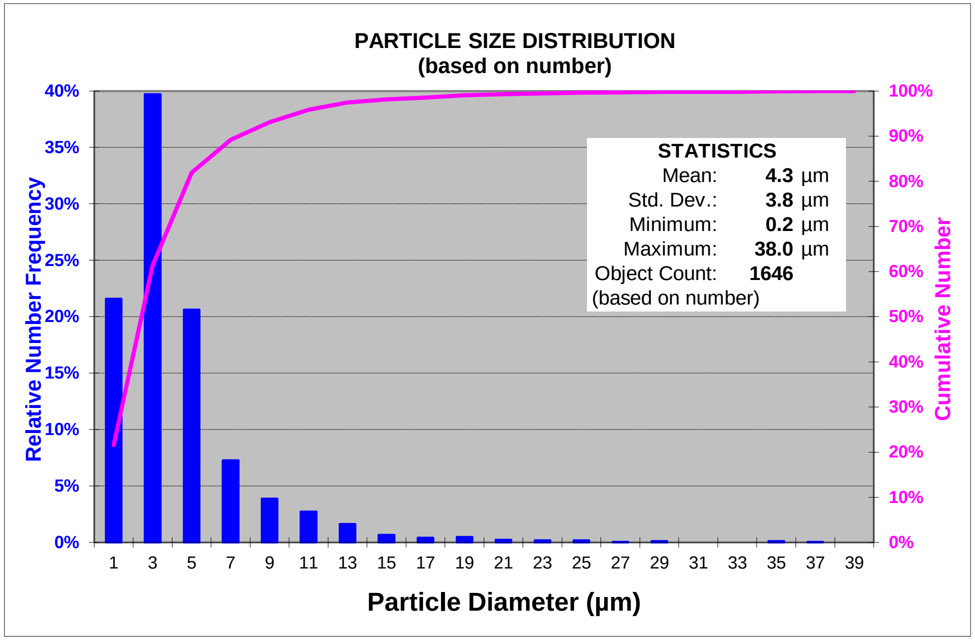
- Spray drier with co-current CO_2 flow
- Nearly instantaneous solid formation
- 50-400 g sample size

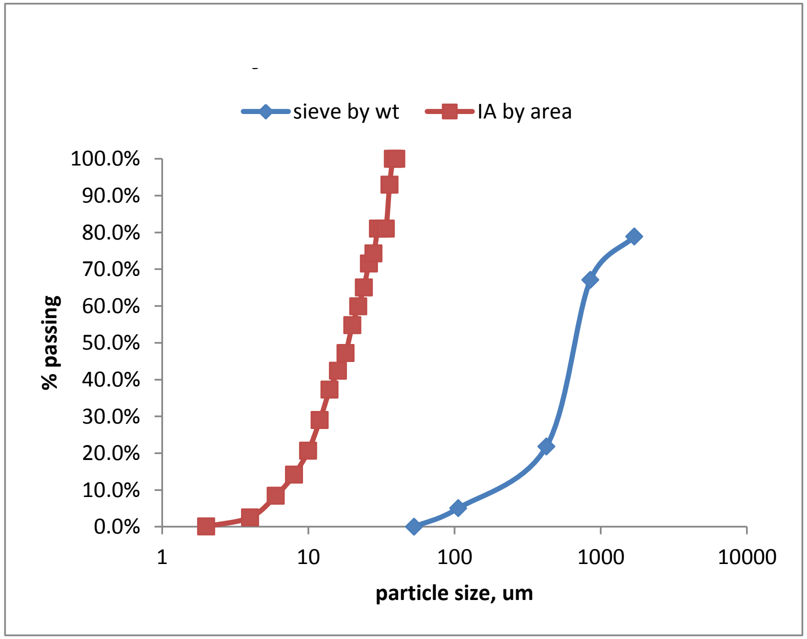
Microscopy of Particles



-Mean particles < 50 µm
-Need to optimize for solid isolation.

PSD by Image Analysis





Mean size = 4.3 um
Aspect ratio 0.6-1.0 (most 0.75-0.9)

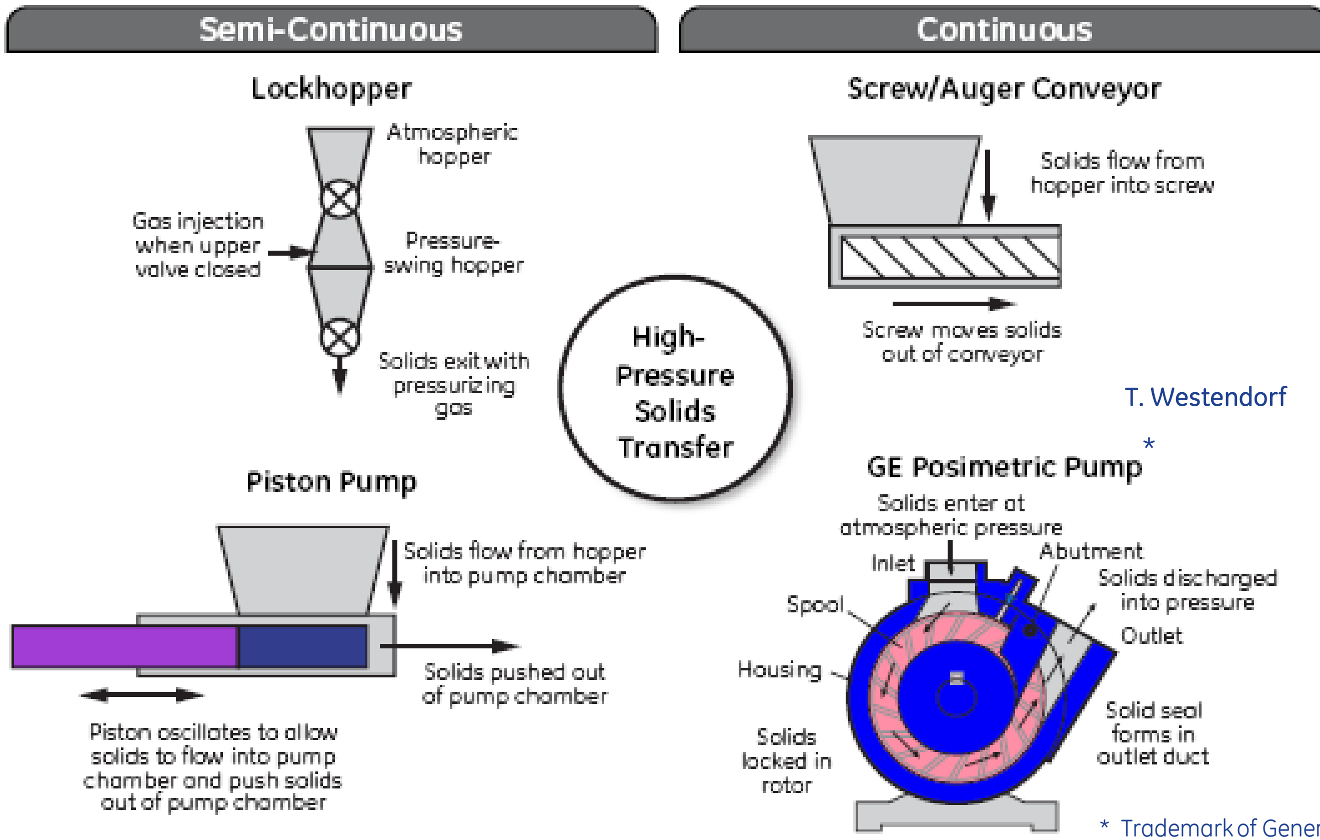
Sieve measures agglomerate size (as expected)

- For solids handling want ~ 500 μm particle size
- Desire larger particles

T. Westendorf
J. Grande

imagination at work

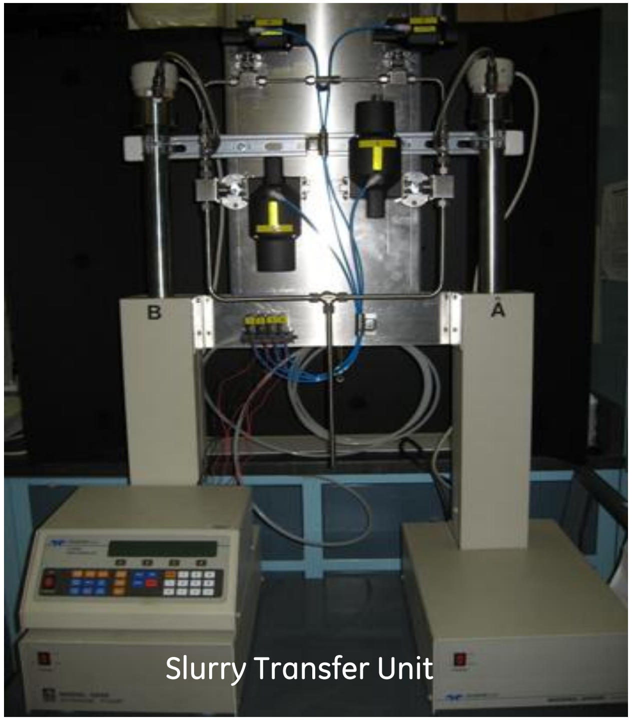
Options for Solid Transport



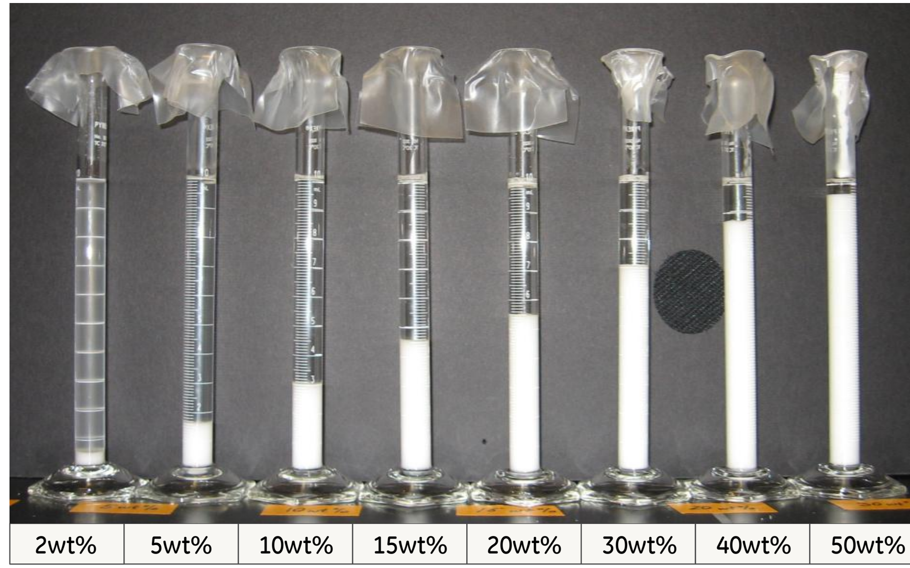
* Trademark of General Electric Company

- Contingent upon physical characteristics of solid
- Density, shape , cohesiveness, moisture content, thermal stability
- Integration between absorber and desorber
- Low pressure to high pressure
- Slurry transport

Slurry Transport



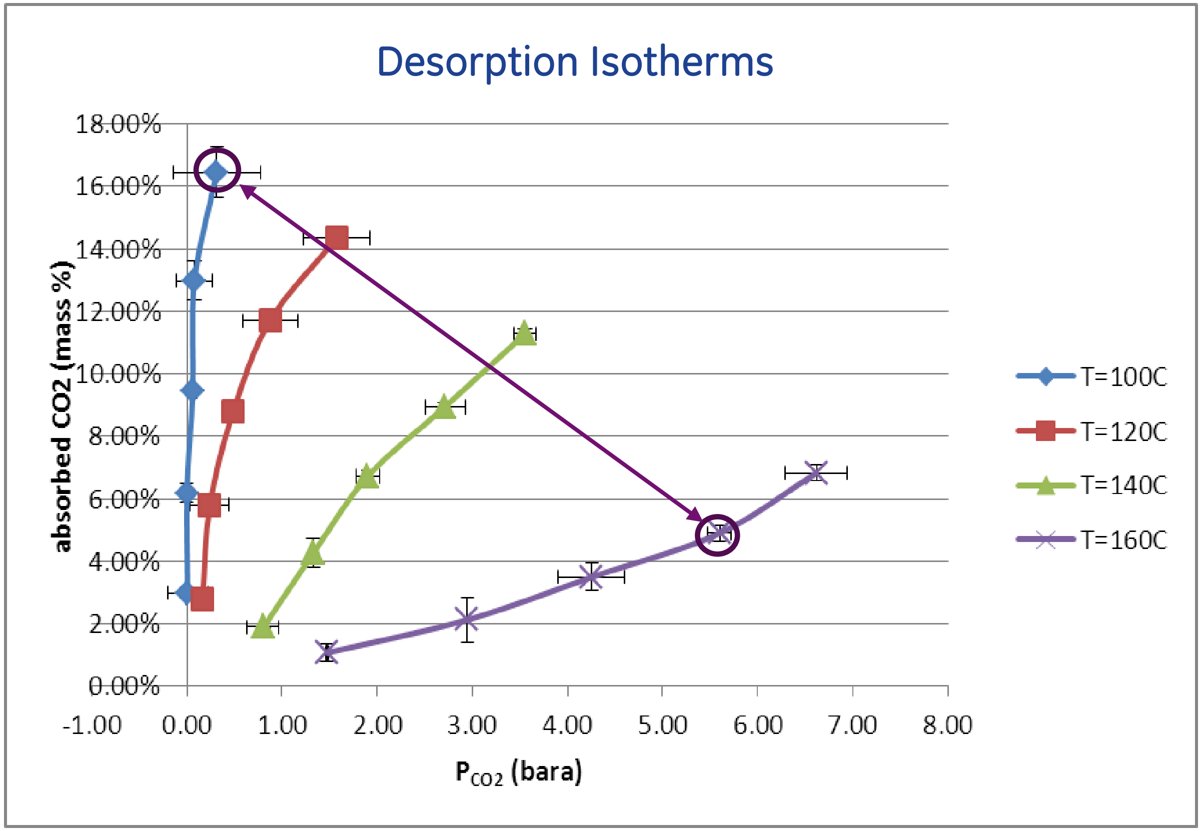
Slurry Transfer Unit



settling of slurry mixtures

- Dual ISCO high pressure pumps
- Pump 50-60 wt % slurry into desorption vessel
- Problem w/ settling and structuring
- Loss of capture capacity

Desorption



R. Farnum
S. Genovese

Error bars = 95% CI

- Neat GAP-0 data
- Rich Solvent >16% CO_2 to Lean Solvent <5% CO_2
- ~11% dynamic range
- CO_2 can be desorbed at relatively high pressure.

Unit Operations

Absorber/spray dryer

- Two spray reactors, 1 w/ MS capability
- Slurry transfer unit with ISCO pumps
- CSTR as high pressure desorption apparatus
- All operations functional
- Next step – integrated system

Slurry Transfer Unit

Desorber Unit

Improvements in Desorption

- Not satisfied with desorption process
- Sacrificing inherent ability of GAP-0
- Revisit solids transport
- Use an extruder as a transport device
- PRISM twin screw extruder

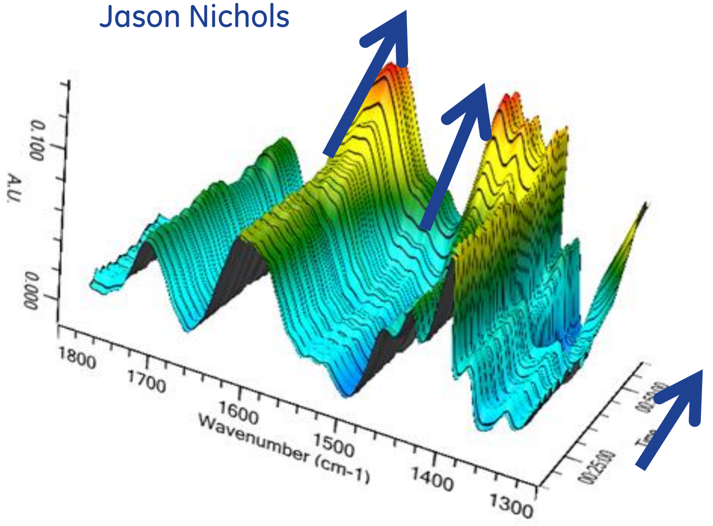

CAUTION
HOT

Further Improvements

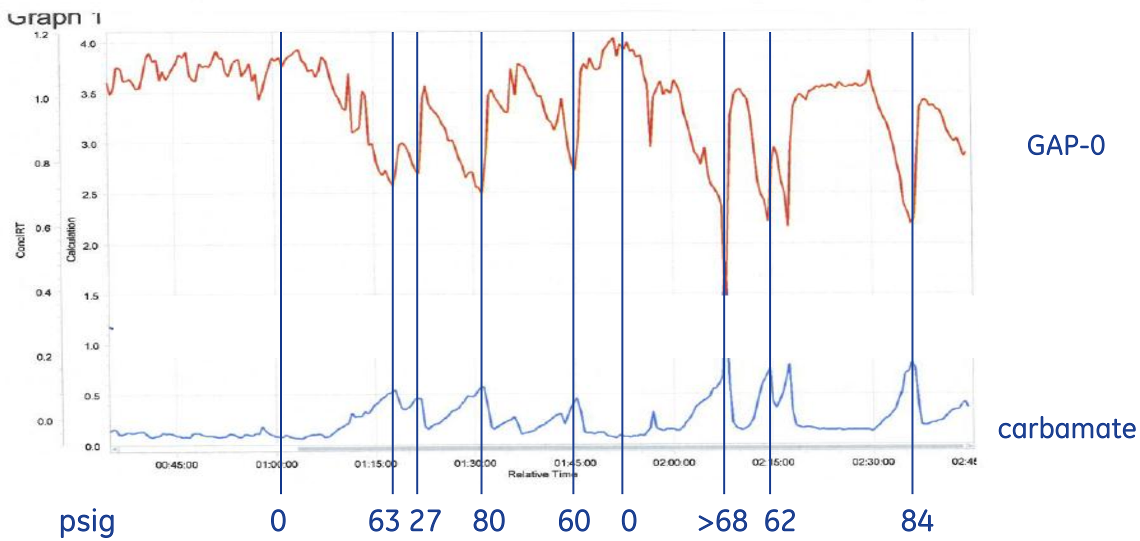
- Take process one step further
- Use extruder to desorb CO_2 from carbamate
- combine 2 unit operations
- save space and money

FT-IR for real time monitoring

Jason Nichols



Increasing pressure

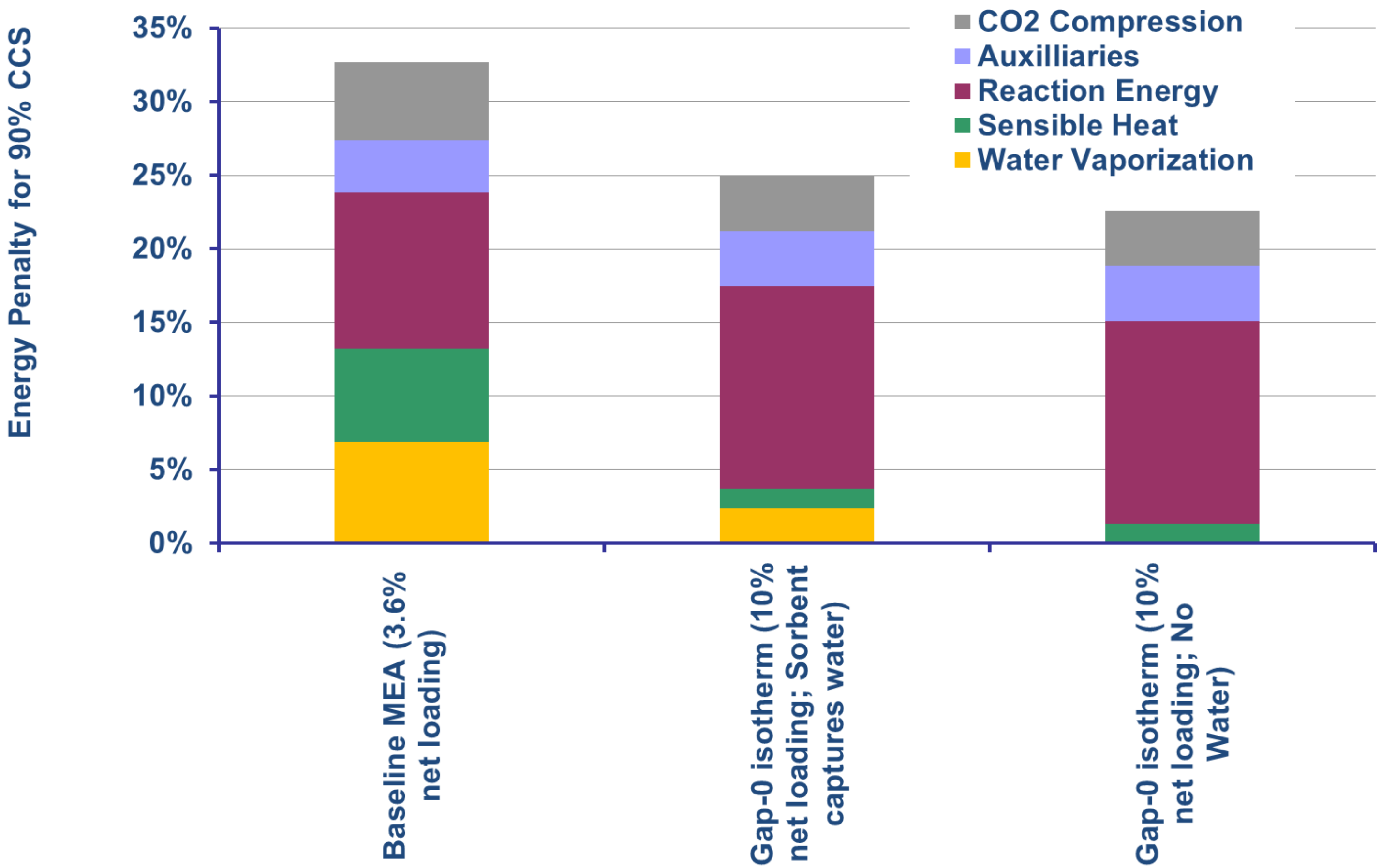


- Effective tool for in-situ monitoring of carbamate formation
- Real time measurement
- Change in intensity of signals related to carbamate concentration

Moving Forward

- Designing and building continuous system
- New, larger absorption unit
- Examining nozzle configurations
- Incorporate extruder into system
- Installing analytical instrumentation
- Gather data for mass balance
- Building ASPEN model for predictive capabilities

Preliminary Energy Penalty Waterfall



R. Vipperla

- Large savings with reduced water
- 24- 32% reduction in energy consumption
- Savings with higher CO_2 pressure

Summary

- Novel use of aminosilicone sorbents for CO_2 capture
- 4th year of effort
- 2 parallel programs ongoing
- Solution-based system in bench-scale phase
- Skid commissioned in Jan 2013
- Unique phase-change process demonstrated
- Designing an integrated system
- Looking for opportunities to leverage this technology in appropriate businesses
- Partner with external industries to validate process(es) and bring value to both

GE GRC CO_2 Capture Team

Thank You